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Characteristics of Produced Water Discharged to the Gulf of Mexico Hypoxic Zone

prepared by
Environmental Assessment Division
Argonne National Laboratory

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Characteristics of Produced Water Discharged to the Gulf of Mexico Hypoxic Zone

for
U.S. Department of Energy
National Energy Technology Laboratory

by
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Executive Summary

Each summer, an area of low dissolved oxygen (the hypoxic zone) forms in the shallow near-shore Gulf of Mexico waters from the Mississippi River Delta westward to near the Texas/Louisiana border. Most scientists believe that the leading contributor to the hypoxic zone is input of nutrients (primarily nitrogen and phosphorus compounds) from the Mississippi and Atchafalaya Rivers. The nutrients stimulate growth of phytoplankton. As the phytoplankton subsequently die, they fall to the bottom waters where they are decomposed by microorganisms. The decomposition process consumes oxygen in the bottom waters to create hypoxic conditions.

Sources other than the two rivers mentioned above may also contribute significant quantities of oxygen-demanding pollutants. One very visible potential source is the hundreds of offshore oil and gas platforms located within or near the hypoxic zone. Many of these platforms discharge varying volumes of produced water. However, only limited data characterizing oxygen demand and nutrient concentration and loading from offshore produced water discharges have been collected. No comprehensive and coordinated oxygen demand data exist for produced water discharges in the Gulf of Mexico.

This report describes the results of a program to sample 50 offshore oil and gas platforms located within the Gulf of Mexico hypoxic zone. The program was conducted in response to a requirement in the U.S. Environmental Protection Agency (EPA) general National Pollutant Discharge Elimination System (NPDES) permit for offshore oil and gas discharges. EPA requested information on the amount of oxygen-demanding substances contained in the produced water discharges. This information is needed as inputs to several water quality models that EPA intends to run to estimate the relative contributions of the produced water discharges to the occurrence of the hypoxic zone.

Sixteen platforms were sampled 3 times each at approximately one-month intervals to give an estimate of temporal variability. An additional 34 platforms were sampled one time. The 50 sampled platforms were scattered throughout the hypoxic zone to give an estimate of spatial variability. Each platform was sampled for biochemical oxygen demand (BOD), total organic carbon (TOC), nitrogen (ammonia, nitrate, nitrite, and total Kjeldahl nitrogen [TKN]), and phosphorus (total phosphorus and orthophosphate). In addition to these parameters, each sample was monitored for pH, conductivity, salinity, and temperature.

The sampling provided average platform concentrations for each parameter. Table ES-1 shows the mean, median, maximum, and minimum for the sampled parameters. For some of the parameters, the mean is considerably larger than the median, suggesting that one or a few data points are much higher than the rest of the points (outliers). Chapter 4 contains an extensive discussion of outliers and shows how the sample results change if outliers are deleted from consideration.

Table ES-1 – Summary of Analytical Data

Parameter	Mean	Median	Maximum	Minimum
BOD, mg/L	957	583	11,108	80
Dissolved BOD, mg/L	498	432	1,128	132
Suspended BOD, mg/L	76	57	146	16
TOC, mg/L	564	261	4,880	26
Dissolved TOC, mg/L	216	147	620	67
Suspended TOC, mg/L	32	13	127	5
Nitrate, mg/L	2.15	1.15	15.80	0.60
Nitrite, mg/L	0.05	0.05	0.06	0.05
Ammonia, mg/L	74	74	246	14
TKN, mg/L	83	81	216	17
Orthophosphate, mg/L	0.43	0.14	6.60	0.10
Total phosphorus, mg/L	0.71	0.28	7.90	0.10
Conductivity, μmhos/cm	87,452	86,480	165,000	360
Salinity, ppt	100	84	251	0
Temperature, ^oC	38	32	80	20
pH, SU	6.29	6.50	7.25	1.77

A primary goal of this study is to estimate the mass loading (lb/day) of each of the oxygen-demanding pollutants from the 50 platforms sampled in the study. Loading is calculated by multiplying concentrations by the discharge volume and then by a conversion factor to allow units to match. The loadings calculated in this study of 50 platforms represent a produced water discharge volume of about 176,000 bbl/day. The total amount of produced water generated in the hypoxic zone during the year 2003 was estimated as 508,000 bbl/day. This volume is based on reports by operators to the Minerals Management Service each year. It reflects the volume of produced water that is generated from each lease, not the volume that is discharged from each platform. The mass loadings from offshore oil and gas discharges to the entire hypoxic zone were estimated by multiplying the 50-platform loadings by the ratio of total water generated to 50-platform discharge volume. The loadings estimated for the 50 platforms and for the entire hypoxic zone are shown in Table ES-2.

Table ES-2 – Loading Estimates for 50 Platforms and Entire Hypoxic Zone

Parameter	Loading from Sampled Platforms (lb/day)	Estimated Loading for Entire Hypoxic Zone (lb/day)
BOD	36,000	104,00
TOC	14,100	40,700
Nitrate	68.3	197
Nitrite	3.07	9
Ammonia	4,770	13,800
TKN	5,140	14,900
Orthophosphate	22.6	65
Total phosphorus	37.6	109

These estimates and the sampling data from 50 platforms represent the most complete and comprehensive effort ever undertaken to characterize the amount and potential sources of the oxygen demand in offshore oil and gas produced water discharges.

Although these numbers appear large, they should be considered in the context of the volume of the hypoxic zone, which is estimated as being 17,000 km^2 in area and an average of 17 m deep. This gives a hypoxic zone volume of 289 km^3 (2.9×10^{11} m^3, or 2.9×10^{14} liters). A discharge loading of 104,000 lb of BOD, if assumed to be evenly diluted throughout the entire hypoxic zone, would contribute only 0.17µg/L, or 0.17 ppb, of additional BOD. The weight of all that water is an equally impressive number. Assuming a weight of 2.2 lb/L (this is the weight of fresh water – salt water is slightly heavier), this equals 6.4×10^{14} lb.

It is also important to consider that offshore platforms discharge to open ocean environments that are subject to wind and wave action. Discharges that are made anywhere near the surface will receive abundant reoxygenation due to the natural processes. More than half of the platforms identified as discharging produced water to the hypoxic zone discharge at or above the surface of the ocean. About 93 percent of those platforms discharge in the top 20 feet of the water column. This should provide effective mitigation for some of the oxygen-demanding pollutants.

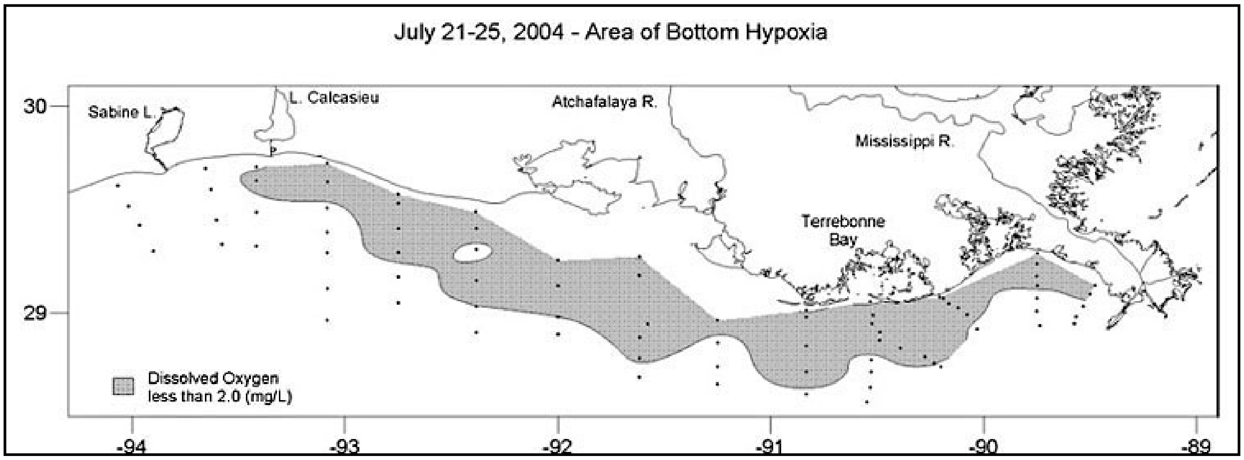
Another important point of perspective is a comparison of the produced water discharge mass loadings to the mass loading of key pollutants from the Mississippi and Atchafalaya Rivers. The produced water discharge loadings estimated for the entire hypoxic zone are several orders of magnitude smaller than those entering the Gulf of Mexico from the rivers. The total nitrogen loading is about 0.16 percent and the total phosphorus loading is about 0.013 percent of the nutrient loading coming from the Mississippi and Atchafalaya Rivers.

Chapter 1 – Introduction

What Is the Hypoxic Zone?

Portions of the northern Gulf of Mexico experience low dissolved oxygen (hypoxia) each summer. A common criterion for hypoxia is a dissolved oxygen concentration of less than 2.0 mg/L. The hypoxic zone in the Gulf of Mexico forms in warm months in the shallow near-shore waters from the Mississippi River Delta westward to near the Texas/Louisiana border. Figure 1 shows the approximate boundary of the hypoxic zone during cruises made in July 2004.

Figure 1 – Boundary of Hypoxic Zone during July 2004 Sampling Cruises

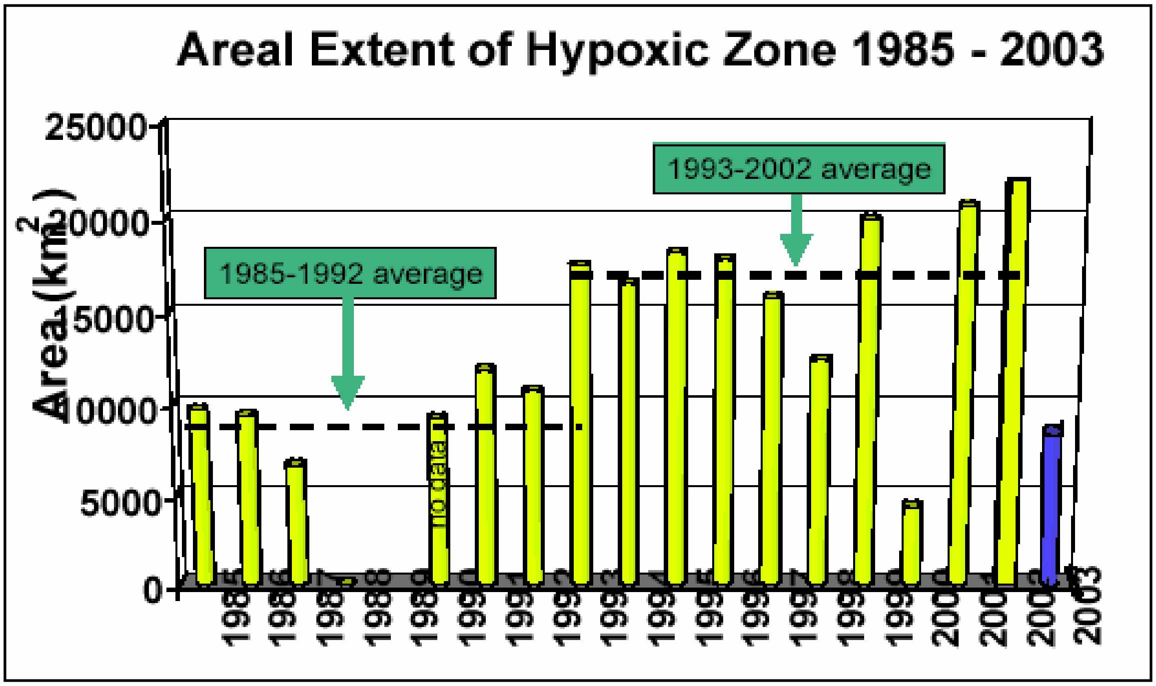


Source: N. Rabalais

Most scientists believe, and the weight of available evidence indicates, that the leading contributor to the hypoxic zone is input of nutrients from the Mississippi and Atchafalaya Rivers. The nutrients stimulate growth of phytoplankton. As the phytoplankton subsequently die, they fall to the bottom waters where they are decomposed by microorganisms. The decomposition process consumes most of the oxygen from the bottom waters to create hypoxic conditions.

The size of the hypoxic zone appears to be increasing over time. Rabalais and others have studied dissolved oxygen levels in this area for nearly 20 years. Figure 2 shows the size of the hypoxic zone by year. The figure shows that the average size from 1985 to 1992 was about 9,000 km^2, while from 1993 to 2002 the average size rose to about 17,000 km^2. Various factors contribute to the size of the hypoxic zone, including river flow (related to upstream rainfall and climate patterns), timing of rainfall in relation to fertilizer application, and changes in point and nonpoint source nutrient loads to the river systems.

Figure 2 – Size of the Hypoxic Zone



Source: N. Rabalais

The presence of hypoxic conditions is undesirable in that it creates an unfavorable habitat for most marine species, particularly those less mobile creatures living near or in the sea floor.

<u>What Is the Issue?</u>

Although the largest contributor to the hypoxic zone is believed to be nutrient inputs from the Mississippi and Atchafalaya Rivers, other sources may also contribute significant quantities of oxygen-demanding pollutants. One very visible potential source is the hundreds of offshore oil and gas platforms located within or near the hypoxic zone. Many of these platforms discharge varying volumes of produced water. Produced water is water trapped in underground formations that is brought to the surface along with oil or gas. Produced water characteristics and physical properties vary considerably depending on the geographic location of the field, the geological formation with which the produced water has been in contact for thousands of years, and the type of hydrocarbon product being produced. Produced water properties and volume can even vary throughout the lifetime of the reservoir.

Traditionally, offshore produced water discharges have been monitored for oil and grease, toxicity, and other parameters. However, only limited data characterizing oxygen demand and nutrient concentration and loading from offshore produced water discharges have ever been collected. No comprehensive and coordinated oxygen demand data exist for produced water discharges in the Gulf of Mexico or anywhere else in the world. The U.S. Environmental Protection Agency (EPA) wants to better understand the contribution that offshore discharges make to the hypoxic zone. The first step toward this goal is collection of oxygen-demand data from a representative sample of platforms. The direct oxygen demand is measured by the 5-day biochemical oxygen demand (BOD) and total organic carbon (TOC). The indirect oxygen demand is measured by the nutrients that stimulate phytoplankton growth – primarily nitrogen and phosphorus.

Concentration data can be combined with discharge volume data to make estimates of the mass loading of oxygen-demanding substances that are discharged within the hypoxic zone. Water quality models can use these data as inputs to estimate the contribution of the produced water discharges compared to the riverine and other sources.

Basis for This Report

On October 7, 2004, EPA Region VI reissued National Pollutant Discharge Elimination System (NPDES) General Permit GMG 290000 for discharges from offshore oil and gas operations in the western portion of the Outer Continental Shelf of the Gulf of Mexico. The permit included a new requirement I. B. 4 (b) (v) for a study of produced water discharges to the hypoxic zone in the Gulf of Mexico (the permit language is displayed in Figure 3). The permit language notes that operators may conduct sampling for each platform individually or may comply with these monitoring requirements through participation in an EPA-approved industry-wide study. The industry, using the Offshore Operators Committee (OOC) as a focal point, elected to conduct the industry-wide study. This report contains the results of that study.

Figure 3 – General Permit Text Describing the Produced Water Hypoxia Study

Two options are available to meet this monitoring requirement. As described below, operators may either conduct the monitoring at each platform or they may participate in an industry wide study to meet the requirements. For the purposes of these monitoring requirements, the hypoxic zone is defined to include the following Minerals Management Service designated lease areas:

> High Island blocks 36, 37, 47, 48, 86, 117, 118, 131, 132, A1, A2, A3, A4, A11, A12, A13, and A14; High Island East Addition blocks 38 through A180; Sabine Pass blocks 5 through 16; West Cameron blocks 154 through 356; West Cameron blocks 22 through 276, East Cameron blocks 10 through 190; Vermillion block 11 through 211; South Marsh Island North Addition blocks 208 through 288; South Marsh Island blocks 1 through 55; Eugene Island blocks 20 through 245, 113A, 113B, 128A, and 129A; Ship Shoal blocks 37 through 211; South Pelto blocks 1 through 25; South Timbalier blocks 7 through 182; Grand Isle blocks 16 through 63; and, West Delta blocks 16 through 101.

Operators discharging produced water from facilities located in the hypoxic zone of the northern Gulf of Mexico, as defined above, shall monitor those discharges for the oxygen demanding parameters and nutrients listed below. Operators shall also submit discharge design information to EPA to be used for analysis of the impacts of the discharges. Monitoring for oxygen demanding pollutants and nutrients shall consist of a minimum of six samples collected at a frequency of once per month. Oxygen Demanding Pollutants - Five-day Biological Oxygen Demand (BOD), Total Organic Carbon (TOC), Nutrients - Ammonia as N, nitrate + nitrite, Total Kjeldahl Nitrogen (TKN), Total phosphorous, and ortho-phosphate. In addition, operators shall provide a description of the outfall structure including the depth of the discharge point, the pipe diameter, the direction in which the discharge is oriented (i.e.: straight down, horizontally, etc.), and the total water depth at the discharge location.

Operators shall also provide an accurate measurement of the volume of produced water which is discharged from each platform located in the hypoxic zone. A report containing the results of these monitoring requirements shall be submitted to EPA Region 6 within nine (9) months after the effective date of this permit. Alternatively, operators may comply with these monitoring requirements through participation in an EPA approved industry-wide study. That study may include a smaller, statistically representative number of discharging platforms.

Chapter 2 – Design and Scope of the Study

EPA requires submittal of the results of the study within nine months of the effective date of the permit (by August 7, 2005). At the time the permit was issued (October 2004), no approved study plan existed. This abbreviated project schedule required a rapid start for the study. It was necessary to move forward expeditiously to develop a study plan that the industry supported; circulate it to EPA, the U.S. Department of Energy (DOE), and the U.S. Department of Interior's Minerals Management Service (MMS) for review and approval; identify the facilities that would be sampled; then commence an intensive sampling program so that sampling could be completed by the end of May 2005. The report was prepared during June 2005 and reviewed during July 2005 in order to meet the August 2005 deadline. This chapter describes the process used to develop the sampling plan, the elements of the plan, and provides a discussion of the data availability and logistical issues that impeded smooth implementation of the plan.

<u>What Events Led to the Study?</u>

During 2003, EPA had circulated an early draft of the general permit that included provisions that would have restricted any new or increased discharges of produced water to the hypoxic zone. The industry, DOE, and MMS objected to these conditions. EPA subsequently replaced this condition with a requirement to collect data on oxygen demand, and the industry and other agencies agreed to help fund studies to characterize the hypoxia problem. DOE's contribution provided funds to Argonne National Laboratory (Argonne) to organize and coordinate this produced water sampling study. Industry funded the analytical work and provided logistical support for the sampling program. MMS provided background data to Argonne and separately funded a white paper on the hypoxic zone. The draft permit was made available for review and comment in June 2004.

A series of meetings and conference calls occurred during the late summer and fall of 2004 that helped to focus the efforts for this study. Two meetings were held in August and September with representatives of the three lead agencies and industry. During the September meeting, the group heard presentations from several scientists about the types of water quality models that could be used to help EPA determine the impacts resulting from platform discharges. The scientists indicated the types of data that they would need from the produced water sampling study to serve as model inputs.

During these meetings, agreement was reached on the actual study area. Rabalais and her co-workers had collected data that showed the approximate boundaries of the Gulf of Mexico areas that experienced at least a 25 percent occurrence of summer hypoxia. These boundaries are shown in Figure 4, which is based on a map prepared by MMS. The lease block listed in the permit language (Figure 3) covers an area slightly larger than the 25 percent-hypoxia boundary. Figure 4 shows a few of the sampled platforms that are located just outside of the 25 percent hypoxia boundary.

The American Petroleum Institute (API) contracted a Louisiana laboratory, AccuLab, to provide analytical services for the study. In order to coordinate large numbers of samples coming from offshore to a series of shore bases, AccuLab partnered with another Louisiana laboratory, Environmental Enterprises, USA, which has an established sample collection and transportation system for offshore samples.

During the next few months, Argonne developed and obtained concurrence for the sampling plan. The details of the final plan are described in this chapter. EPA approved the sampling plan on February 2, 2005. Argonne, in conjunction with representatives from OOC and API, finalized selection of the platforms that would be sampled, notified those platforms operators, and began sampling in late February.

Late in 2004, the OOC established a Web-based registry so that its members and other offshore operators could enter information on their platforms that had discharges in the hypoxic zone. This registry was later used to select platforms to be sampled.

Elements of the Sampling Plan

What parameters should be sampled? The goal of the study is to better understand the direct and indirect oxygen demand associated with produced water. The direct oxygen demand was measured on all samples by BOD and TOC. To aid the modelers, in approximately 10 percent of the samples, separate tests were done to distinguish between the dissolved and particulate forms of oxygen-demanding materials (e.g., particulate BOD, dissolved BOD, dissolved organic carbon, and particulate organic carbon).

The indirect oxygen demand was measured by the nutrients that stimulate phytoplankton growth – nitrogen and phosphorus. For nitrogen, samples were tested for ammonia, nitrate, nitrite, and total Kjeldahl nitrogen (TKN). For phosphorus, samples were tested for total phosphorus and orthophosphate. In addition to these highlighted parameters, each sample was monitored for basic water quality parameters (e.g., pH, conductivity, salinity, and temperature).

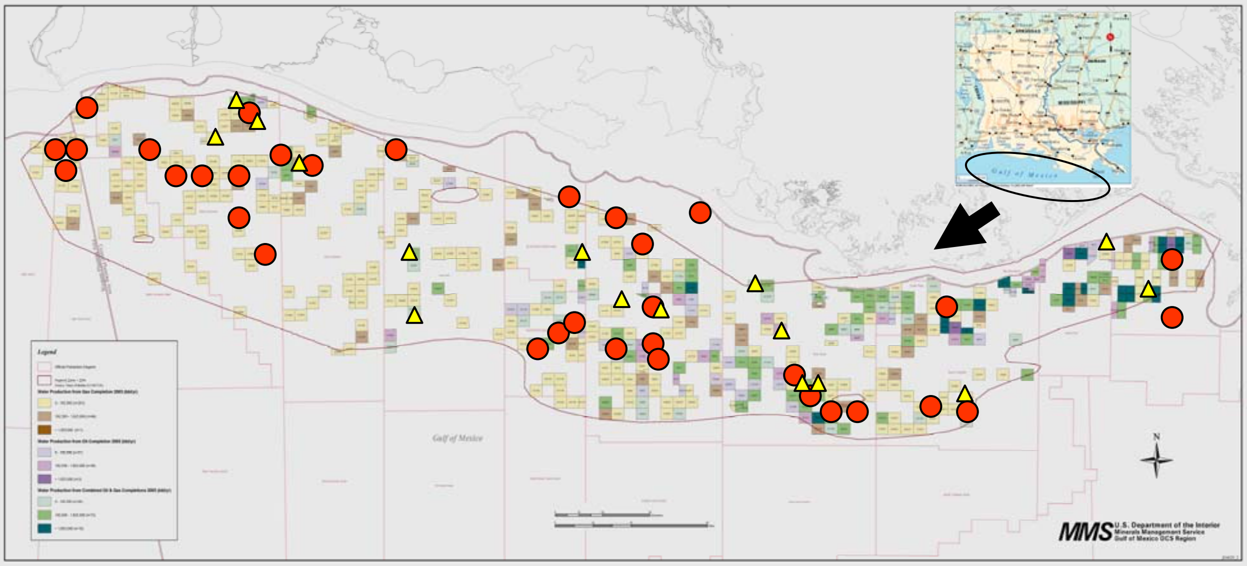
EPA's *Methods for the Chemical Analysis of Water and Wastes* was used to perform the required analyses. The parameters assayed and tests methods used in this study are shown in Table 1.

Table 1 – Analytical Methods Used in the Study

Test Parameter	EPA Method
BOD	EPA Method 405.1
TOC	EPA Method 415.1
TKN	EPA Method 351.3
Ammonia	EPA Method 350.3
Nitrate	EPA Method 353.3
Nitrite	EPA Method 354.1
Orthophosphate	EPA Method 365.2
Total phosphorus	EPA Method 365.2
pH	EPA Method 150.1
Salinity	EPA Method 325.3
Conductivity	EPA Method 120.1

What basis was used to select the sites? Neither EPA nor MMS has readily available information on the number of produced water discharges made to the study area. As an alternate approach, MMS data on those leases that generate (not discharge) produced water was used. MMS reported 496 leases in the study area that showed both production of oil and/or gas and water in 2003. It was not practical to sample the discharges in all of the leases, so a representative subset of about 10 percent of the leases was chosen. The study focuses on 50 sites located within a zone having at least a 25 percent occurrence of summer hypoxia based on average annual data from 1985 to 2002 (the >25 percent hypoxic zone). Figure 4 shows the >25 percent hypoxic zone boundary, the leases and lease blocks, and the locations of the 50 platforms selected for sampling.

Figure 4 – Location of Platforms in Sampling Study



● Platforms sampled one time and selected at random.

△ Platforms sampled three times and selected based on discharge volume and type of hydrocarbon produced.

As shown in Figure 4, two of the platforms fall just outside of the >25 percent hypoxia boundary. This reflects the fact that the list of lease blocks in EPA's permit language (Figure 3) covers an area slightly larger than the >25 percent hypoxia boundaries. Nevertheless, these platforms are very close to the boundary and could potentially influence conditions inside the boundary.

A hybrid sampling approach was followed to meet EPA's goals of large enough sample size, an estimate of temporal variability, and completion of the sampling program in a short time frame. Sixteen sites were scheduled for sampling three times each at about one-month intervals, and an additional 34 sites were scheduled to be sampled once. One of the 16 platforms stopped producing water before the third sample was collected, so only two samples were available at that location. The sites to be sampled once were selected at random, while the sites to be sampled three times were selected using the following criteria to ensure a range of different production and discharge conditions.

> **The produced water generation rate**. Produced water discharge composition may vary between platforms having different volumes of discharge. Platforms with large discharges may use different types of treatment processes than platforms with smaller discharges. To evaluate the effect of produced water volume, the produced water generation rate by lease was tentatively subdivided into three classes: low production (<500 bbl/day), medium production (500 to 5,000 bbl/day), and high production (>5,000 bbl/day). Generation rates were initially determined using MMS records for 2003, but were later refined by obtaining actual discharge data from the selected operators.

> **The nature of the hydrocarbon that is produced on the lease generating the produced water**. Produced water associated with gas production may have different chemical composition than produced water from oil wells. Hydrocarbon production is subdivided into three classes: leases having wells with >90 percent oil completions, leases having wells with >90 percent gas completions, and leases having wells with both oil and gas completions (i.e., from 10 percent to 90 percent oil completions). This type of subdivision also leads to wide geographic coverage of selected sites throughout the hypoxic zone. Wells in the eastern portion of the MMS Central Planning Area of the Gulf of Mexico tend to produce more oil, while those in the western Gulf produce more gas.

Subdividing by these two factors results in 9 categories. Representative leases were selected from 8 of the 9 categories (generally among the highest 5 water-producing leases in each category). No platforms fell into the high water production/gas category. This is not surprising because, in general, gas wells do not produce as much water as oil wells. Sixteen leases operated by 6 different companies were selected (Table 2). The operators were contacted to verify their information and to identify which platform on the lease would be sampled.

For the other 34 platforms to be sampled once, leases were randomly selected from a list of platforms entered into the OOC hypoxia study registry. From the full list of platforms, platforms or leases that had already been sampled for the three-time sampling program were deleted. A short list was developed by randomly selecting 50 sites from the list. The first 34 platforms were selected and then contacted. Several of the platforms were not producing any water during the short time window that the sampling program needed to follow. These were replaced by the next platform in order from the list of 50. The final list of one-time sampled platforms is shown in Table 3. The 50 platforms represent 22 different companies and are located in 10 different lease areas.

Table 2 – Platforms Sampled Three Times

Platform[a]	Operator
EC 47JP	Newfield
EI 107A	Apache
EI 95F	W&T Offshore
GI 19#3	ExxonMobil
SM 268A	Apache
SS 108D	ChevronTexaco
SS 169C	ChevronTexaco
SS 182C	ChevronTexaco
SS 58A	Newfield
ST 148E	Newfield
VR 164A	ExxonMobil
VR119D	W&T Offshore
WC 102G	BP
WC 110A	BP
WC 65JA	BP
WD 73A	ExxonMobil

[a] The two-letter abbreviations are used by MMS for its lease areas. Each lease area is subdivided into a series of numbered blocks, which are typically three miles by three miles in size. Not each lease block has a platform; however, if there is more than one platform or structure on a lease block, each structure is given an ID, usually a letter designator. For example, SS 182C is platform C on block 182 of the Ship Shoal lease area.

How much variability is acceptable between the three samples taken at each of the 16 platforms? Before starting the sampling, the project participants agreed that at the end of the three-time sampling program, Argonne would evaluate the BOD results at each platform using a variability criterion. The criterion proposed by Argonne and approved by EPA is a coefficient of variation (CV) of 0.6 or lower. The CV is defined as the standard deviation divided by the mean. EPA has based much of its water quality control program on the 1991 *Technical Support Document for Water Quality-Based Toxics Control* (TSD). On page 107 of the TSD, EPA states: "EPA recommends a value of 0.6 as a default CV, if the regulatory authority does not have more accurate information on the CV for the pollutant or pollutant parameter." This same general principle is embodied in the November 2004 draft *National Whole Effluent Toxicity (WET) Implementation Guidance Under the NPDES Program*, which recommends the use of CV = 0.6 for sample sizes of less than 10.

After the third sample was collected from a platform, the mean, standard deviation, and CV were calculated for each platform. If the first three samples exceed the variability criterion, a fourth sample is taken and the variability is checked again. If the data meet the variability criterion, sampling stops. If the data do not meet the variability criteria, a fifth sample is taken. The same procedure is used following the fifth sample to determine if a sixth sample if necessary.

Table 3 – Platforms Sampled One Time

Lease Area, Block, and Platform ID	Operator
EC 46B	Stone Energy Corporation
EC 49B	Newfield Exploration Company
EI 128A-JC	Energy Resource Technology, Inc.
EI 172A	Newfield Exploration Company
EI 175B	Apache
EI 184A	Newfield Exploration Company
EI 50-1	Hunt Petroleum (AEC), Inc.
EI 57A	Northstar Gulfsand, LLC
EI 74A	Chevron U.S.A. Inc.
HI 37A	Seneca Resources Corporation
HI 39A	The Houston Exploration Company
HI 46A	Mariner Energy, Inc.
SM 238-190	El Paso Production GOM Inc
SM 23G	Devon Energy Production Company L.P.
SM 33D	Apache
SM 40 JA	Hunt Petroleum (AEC), Inc.
SS 157A	Newfield Exploration Company
SS 182E	Chevron U.S.A. Inc.
SS 189A	Apache
SS 191 B	Hunt Petroleum (AEC), Inc.
ST 161A	Apache
ST 164C	Stone Energy Corporation
ST 34A	Bois d'Arc Offshore Ltd
VR 22B	Energy Resource Technology, Inc.
WC 130A	Dominion Exploration & Production, Inc.
WC 168A	Linder Oil Company, A Partnership
WC 170A	Nexen Petroleum
WC 173K	The Houston Exploration Company
WC 215A	Energy Resource Technology, Inc.
WC 237A	ATP Oil & Gas Corporation
WC 53A	El Paso Production
WC 71D	BP Exploration & Production Inc.
WD 45A	Nexen Petroleum USA Inc.
WD 89A	Eni Petroleum Co. Inc.

Who collected the samples and how did they get transported to the laboratory? The samples were collected by the operators of each selected offshore platform. Environmental Enterprises USA (EEUSA) prepared the sample kits, with sample bottles, preservatives where needed, a thermometer, sampling instructions (Appendix A), a sampling log sheet (Appendix B), and a chain-of-custody form (Appendix C). EEUSA scheduled the sample dates with each operator.

The sample kits were delivered by an EEUSA courier to the shore bases used by each company several days in advance of the sampling date.

The operators transported the sample kits to the platforms by helicopter or work boat. On the scheduled sampling date, the operators collected the samples (they had been instructed to first let the produced water sampling outlet on each platform run for several minutes to remove standing water), packaged them on ice in a cooler, and passed them over to helicopter pilots or workboat staff to bring to the shore base. Most samples were picked up from the shore bases by the EEUSA courier on the same day or the day following sampling and were driven to AccuLab. In a few cases, the samples were sent to AccuLab by overnight delivery services or by local courier services. The transportation needed to be closely coordinated because several of the analytical methods used required that the tests be started no later than 48 hours following sample collection.

Although sampling was fairly simple, the logistics involved were quite complicated, considering the offshore location of the sampling points, the distance to the laboratory, and preservation requirements/hold times associated with several of the analytical parameters. Table 4 indicates the maximum sample hold times and preservative requirements for each parameter.

Table 4 – Hold Times and Preservative Requirements

Test Parameter	Hold Time (from date and time of sample collection)	Preservative Requirements
BOD	48 hours	Cool, < 4°C
TOC	28 days	H_2SO_4 to pH <2; Cool, <4°C
TKN	28 days	H_2SO_4 to pH <2; Cool, <4°C
Ammonia	28 days	H_2SO_4 to pH <2; Cool, <4°C
Nitrate	48 hours	Cool, <4°C
Nitrite	48 hours	Cool, <4°C
Orthophosphate	48 hours	Cool, <4°C
Total phosphorus	28 days	H_2SO_4 to pH <2; Cool, <4°C
pH	15 minutes	None required
Salinity	28 days	None required
Conductivity	28 days	Cool, <4°C

What type of quality assurance/quality control (QA/QC) measures were included in the study design? Argonne, in conjunction with API, OOC, EEUSA, and AccuLab, developed sample collection and handling instructions, a chain-of-custody form, and a sampling log sheet. These are included as Appendices A, B, and C, respectively. The study included two types of field controls: field blanks and field duplicates. In order to validate field activities, the sampling program included field blanks for about 25 percent of the samples. The purpose of the field blank is to assess the possible impact of the sampling and transportation process on the quality of data collected. If any blank test result is above the maximum quantitation level (MQL) for any test parameter in the field blank, the reason is typically investigated and appropriate corrective action is taken as soon as possible, particularly if multiple blanks systematically show the same type and level of contamination.

Field duplicates were collected for about 10 percent of the samples. A field duplicate is a sample collected at the same time and under the same conditions as an actual sample. The purpose of field duplicate samples is to assess precision and the variability of the discharge stream. If a pair of duplicate samples exhibits a relative percent difference (RPD) of greater than 25 percent, investigation of the cause and documentation of the findings are considered, particularly if multiple duplicates consistently demonstrate high RPDs for the same parameter.

AccuLab has its own laboratory QA/QC program for ensuring that samples are received and handled correctly, and that instruments are calibrated. At the time of laboratory receipt, technicians log-in the samples, verify chain-of-custody information against the sample bottles, check for sample integrity (leaking, broken bottles, or improper preservation, etc.), and measure the temperature of the coolers to ensure that the samples were <4°C. If samples had not had sufficient time to cool prior to arrival, the presence of ice in the container in which the samples arrive was interpreted as evidence that the chilling process had begun. Sample temperature is particularly important for the BOD measurement, given that the rate of biodegradation will increase with increasing temperatures. The pH of samples preserved with acid or base was also checked.

Discrepancies during sample receipt are noted on AccuLab's Sample Receipt Checklist form and also on AccuLab's Sample Problems Fax Back form. The latter form identifies problems with a sample or a shipment of samples and allows the client two options: 1) discard samples, or 2) proceed with analysis with the understanding that any discrepancies might be flagged on the laboratory report. After discrepancies are resolved, the samples are logged into the Laboratory Information Management System (LIMS) and processing begins.

Prior to analysis, individual instruments required for each analysis were calibrated in accordance with manufacturers' instructions as well as laboratory-specific standard operating procedures (SOPs). This includes initial calibration as well as continuing calibration verification. Recalibrations are performed as necessary. Analyses were then performed in accordance with method requirements and laboratory SOPs. Laboratory QC samples consisted of the following:

> ***Laboratory Reagent Blanks (LRB):*** These are also called method blanks. An LRB is a sample of deionized water and is analyzed as an actual sample. They are used to show the analysis process to be free of contamination. An LRB is analyzed with every batch of samples (a batch of samples is 20 or fewer samples analyzed within a 24-hour period). Sample analyses do not begin until the LRB result is below the MQL for the analyte tested. An exception is made for BOD. If the oxygen depletion of the unseeded dilution water is greater than 0.2 mg/L, the BOD result is flagged. In this case, the data point is treated as estimated rather than as a definitive data point.

> ***Laboratory Control Sample (LCS):*** These are also called laboratory-fortified blanks. An LCS is prepared by adding a known amount of analyte to deionized water. The LCS is analyzed as an actual sample. They are used to assess accuracy

and to assure that the method and techniques used are capable of producing data of acceptable quality. An LCS is analyzed with every batch of samples. In general and in the absence of method-specific guidance, the acceptance limits for LCS recovery is 80-120 percent of the LCS true value. If the recovery of an LCS is outside of the acceptance range, sample analysis is halted until the cause is determined and corrected. Samples associated with a defective LCS are reanalyzed if possible. In the case of BOD, where reanalysis is generally not possible due to hold times, the results for samples associated with the defective LCS are flagged.

Matrix Spike (MS) Sample: An MS sample is prepared by adding a known amount of analyte to an actual sample. The MS is analyzed as an actual sample. MSs are used to assess the effect of sample matrix on a particular analysis. An MS is analyzed with every batch of samples. Given that samples from different projects are often combined to form a batch, it is possible that some MS samples may represent a different client or project. The laboratory indicated that it would strive to include MS samples from the produced water study as part of the batch QC. In general and in the absence of method-specific guidance, the acceptance limits for MS recovery is 80-120 percent of the spike concentration. If recovery is outside the acceptance limits and the LCS recovery is within limits, the results associated with the out-of-range MS are flagged. Note that the nature of the BOD test precludes the analysis of spiked samples.

Matrix Spike Duplicate (MSD) Sample: An MSD sample is prepared and analyzed in exactly the same manner as an MS sample. MSD samples are used to assess the precision of an analysis and naturally take matrix effects into account. An MSD is analyzed concurrently with the MS. In general and in the absence of method-specific guidance, the acceptance limits for MS/MSD is ≤25 percent RPD. If the RPD of an MS/MSD pair is >25 percent, the associated results are flagged. For BOD, the LCS is analyzed in duplicate (a laboratory control sample duplicate, or LCSD) and serves as the precision assessment for the method.

What logistical and policy issues created extra challenges? Several features of this sampling program presented challenges above and beyond the normal complicating factors of field work. The first issue was the compressed time table. EPA required that the report be completed and submitted within nine months of the effective date of the permit. This is much shorter than normally used to design and conduct a study of this magnitude.

A second important issue is the remote locations of the platforms and the shore bases and the need to coordinate several transportation legs and still meet maximum sample holding times. Sample delivery relied heavily on helicopters. Particularly in the early weeks of the sampling, the Gulf of Mexico experienced many foggy days, and planned sampling dates needed to be rescheduled.

Another important factor is the presence of numerous project participants. The study plan had to be reviewed and approved by three agencies and by industry (through the OOC) before it could be implemented. This process required several iterations of review and revision of the sampling plan.

Ideally, sampling for all platforms would have been done by the same person or teams of people. This was not possible for this study due to logistical concerns and related costs. Once the sampling began, it was necessary to involve personnel from many different oil and gas companies. Often a company's permitting point of contact was not the person who does the field sampling, so there was a need to answer questions and educate many persons about the importance and details of the study. Further, there were many intermediate steps in the chain of custody, such as helicopter pilots and shore base managers.

Scheduling presented a major challenge. Quite a few of the original sampling dates needed to be postponed for a few days because of bad weather, maintenance on platform equipment, or other reasons. The EEUSA courier has a fixed weekly shore base visitation schedule. With the large number of delays, samples often came to shore on days other than the regularly scheduled collection days. The EEUSA scheduling coordinator worked very diligently to reschedule all samples within the sample holding time window.

Several platforms were producing water when the schedule was developed, but on the scheduled sampling date no water was being produced. These needed to be rescheduled or other platforms sampled, when the water production was not likely to resume soon. One of the platforms that was scheduled for three-time sampling was sampled on the first two dates as planned. By the time its third sampling date came around, the platform had stopped producing water and was not anticipated to resume production any time soon. Because the sampling cycle was so far along, only two samples were collected at that platform.

Chapter 3 – Description of Platforms Selected for Sampling

This chapter provides several types of information about the 16 platforms selected for three-time sampling and the 34 platforms selected for one-time sampling. This information is included to meet the general permit requirements and to serve as reference information for the water quality models that are scheduled to be run.

<u>Platform Location and Discharge Configuration</u>

The general permit language requires submission of information about the discharge design of each of the tested platforms. That information and the latitude and longitude of each platform are included in Table 5.

Table 5 – Platform Discharge Design and Location

Platform	Water Depth (ft)	Discharge Depth (ft below surface)	Pipe Diameter (in.)	Pipe Orientation	Diffuser	Latitude	Longitude
EC 46B	45	6	6	Vertical down	None	29.446784	–92.971174
EC 47JP	50	6	6	Vertical down	None	29.440641	–92.977681
EC 49B	50	0	4	Vertical down	None	29.414894	–92.899125
EI 107A	25	5	4	Vertical down	None	29.026494	–91.527274
EI 128A-JC	55	2	6	Vertical down	None	28.94315	–91.609364
EI 172A	78	10	4	Vertical down	None	28.786711	–91.589594
EI 175B	67	5	8	Down	None	28.790828	–91.731624
EI 184A	88	70	6	Vertical down	None	28.732422	–91.607955
EI 50-1	23	0	4	Vertical down	None	29.2313717	–91.75488895
EI 57A	8	10	4	Vertical down	None	29.244395	–91.386834
EI 74A	18	0	4	Vertical down	None	29.140763	–91.63893
EI 95F	17	2' above	8	Vertical down	None	29.08748886	–91.6988907
GI 19#3	55	41	12	Up	Yes[a]	29.149858	–89.897425
HI 37A	40	0	6	Vertical down	None	29.46958595	–93.90923728
HI 39A	35	0	6	Vertical down	None	29.478029	–93.796791
HI 46A	30	0	4	Vertical down	None	29.42128298	–93.84003778
SM 238-190	10	4	8	Horizontal	None	29.32831734	–91.88724812
SM 23G	81	8	4	Vertical down	None	28.86716564	–91.89783564
SM 268A	30	10	6	Vertical down	None	29.115855	–91.871104
SM 33D	85	0	4	Down	None	28.827329	–91.947355
SM 40 JA	97	6	6	Vertical down	None	28.80942007	–92.05837548
SS 108D	25	0	18	Vertical down	None[b]	28.859204	–91.131668
SS 157A	52	0	6	Vertical down	None	28.67438498	–91.08369876
SS 169C	60	32	6	Vertical down	Yes[c]	28.644791	–91.026014
SS 182C	65	1	6	Vertical down	None	28.618316	–90.994974
SS 182E	65	18	6	Vertical down	Yes[d]	28.619125	–90.994825
SS 189A	85	0	6	Down	None	28.564446	–90.803085
SS 191 B	72	0	4	Vertical down	None	28.58814302	–90.90229214
SS 58A	20	0	3	Vertical down	None	28.982503	–91.218691
ST 148E	96	2	4	Vertical down	None	28.58847484	–90.42093781
ST 161A	125	0	4	Vertical down	None	28.569312	–90.408951
ST 164C	100	0	8	Vertical down	None	28.56943	–90.545117
ST 34A	50	5	6	Vertical down	None	28.914125	–90.486815
VR 164A	95	77	8	Vertical down	None	28.902763	–92.488892

Platform	Water Depth (ft)	Discharge Depth (ft below surface)	Pipe Diameter (in.)	Pipe Orientation	Diffuser	Latitude	Longitude
VR 22B	38	0	4	Vertical down	None	29.469399	–92.549909
VR119D	68	5' above	4	Vertical down	None	29.12059	–92.502505
WC 102G	42	0	4	Vertical down	None	29.559159	–93.14566
WC 110A	40	6	4	Vertical down	None	29.518285	–93.284358
WC 130A	40	8	2	Vertical down	None	29.48589141	–93.5109452
WC 168A	43	10	6	Vertical down	None	29.407099	–93.404965
WC 170A	40	6	6	Vertical down	None	29.400442	–93.331788
WC 173K	60	10	2	Vertical down	None	29.39874631	–93.17797896
WC 215A	60	6	6	Vertical down	None	29.243337	–93.178322
WC 237A	110	30	4	Vertical down	None	29.107708	–93.085114
WC 53A	35	10	2	Horizontal	None	29.624477	–93.750615
WC 65JA	36	10	4	Vertical down	None	29.627548	–93.172415
WC 71D	38	0	4	Vertical down	None	29.592809	–93.148724
WD 45A	45	5	4	Vertical down	None	29.10861	–89.643752
WD 73A	168	36	8	Vertical down	Yes[e]	28.946315	–89.706342
WD 89A	200	10	7	Vertical down	None	28.901085	–89.614413

[a] The 12" downcomer departing the platform runs to 3' below the sea floor, where it is extended horizontally, then turned upward to provide for three 6" discharge ports located at least 100 meters apart.
[b] Vertically split pipe with 2 ports, one above the water and one below, separated by 25'.
[c] 2 ports separated by 22'.
[d] Ports separated vertically by 22'.
[e] Consists of a vertical 8" pipe with an 8" discharge port (50 percent flow discharged horizontally to pipe) at 8' below the sea surface and a second 8" discharge point at the end of the pipe (discharging down toward the seafloor with 50 percent flow) located 36' below the sea surface.

Produced Water Discharge Volume

The general permit language also requires submission of information about the discharge volume of each of the tested platforms. Specifically: “Operators shall also provide an accurate measurement of the volume of produced water which is discharged from each platform located in the hypoxic zone.” Some platforms have relatively consistent discharge volume while others fluctuate a great deal. Most discharges are composites of produced water from numerous wells from one or more platforms. The individual wells may be completed in different formations with different water production rates. Over time, some wells go out of service and other ones come online. All of these factors contribute variability to discharge volumes and characteristics.

Table 6 shows the monthly discharge volumes from eight platforms that discharge into the hypoxic zone. Several of these are part of the group of 50 sampled platforms. Data are presented by month for three years for three of the platforms and for one year for five of the platforms. The statistical features include mean, standard deviation, minimum, and maximum. It is apparent that volumes are not consistent at most of these platforms. For the purposes of this report, we used the average value to characterize the flow for these platforms. Nevertheless, readers should recognize that discharge volumes fluctuate substantially over time.

Table 6 – Variability in Water Production at 8 Gulf of Mexico Platforms over Many Months

Month	Discharge Volume (bbl/day) from Platforms Identified Below							
	A	B	C	D	E	F	G	H
Apr-03	20,632	77	56,140	No data	No data	No data	No data	No data
May-03	18,603	94	58,075	No data	No data	No data	No data	No data
Jun-03	21,610	101	62,330	No data	No data	No data	No data	No data
Jul-03	20,913	69	65,173	No data	No data	No data	No data	No data
Aug-03	17,214	127	68,788	No data	No data	No data	No data	No data
Sep-03	16,679	125	70,525	No data	No data	No data	No data	No data
Oct-03	16,048	78	71,252	No data	No data	No data	No data	No data
Nov-03	17,095	84	70,376	No data	No data	No data	No data	No data
Dec-03	18,000	87	70,468	No data	No data	No data	No data	No data
Jan-04	19,238	90	49,021	No data	No data	No data	No data	No data
Feb-04	20,071	110	61,527	No data	No data	No data	No data	No data
Mar-04	19,857	67	69,799	No data	No data	No data	No data	No data
Apr-04	19,996	36	68,568	No data	No data	No data	No data	No data
May-04	20,697	57	63,544	No data	No data	No data	No data	No data
Jun-04	20,862	96	63,008	No data	No data	No data	No data	No data
Jul-04	18,774	2	66,642	7,750	34,809	32,000	30,655	9,547
Aug-04	19,983	71	66,085	8,000	32,358	33,000	30,495	9,624
Sep-04	19,057	157	53,503	9,584	33,358	25,880	15,332	10,287
Oct-04	26,442	246	63,244	9,869	32,780	28,000	16,386	10,509
Nov-04	22,560	528	60,931	9,591	34,811	30,000	5,306	795
Dec-04	22,618	856	63,038	9,100	32,032	26,151	4,344	8,641
Jan-05	22,911	921	61,309	8,450	35,106	26,400	25,236	8,750
Feb-05	19,297	522	64,200	6,440	35,600	25,900	31,057	10,400
Mar-05	22,190	558	64,363	8,000	35,000	21,387	33,490	10,442
Apr-05	21,288	620	62,398	5,540	33,800	24,530	34,908	9,011
May-05	21,505	589	65,212	6,451	32,500	24,500	32,243	10,237
Average	20,159	245	63,828	8,070	33,832	27,068	23,587	8,931
Std. Dev.	2,270	270	5,407	1,444	1,286	3,440	11,322	2,787
Minimum	16,048	2	49,021	5,540	32,032	21,387	4,344	795
Maximum	26,442	921	71,252	9,869	35,600	33,000	34,908	10,509

Table 7 shows discharge volume figures provided by individual companies as part of their registration on the OOC hypoxia registry website during the winter of 2004-2005. It is not possible to tell how the companies derived this number. It could have been a long-term average, the average of the most recent quarter, a long-term maximum, or some other value. Most likely, different companies employed different approaches. In mid-July 2005, each operator was asked to review the previously submitted data and make sure the volume was representative of an annual average expressed as bbl/day. Updated or confirmed data were received from some but not all of the companies. In order to meet the report submittal deadline, the report was completed using the best available estimates of discharge volumes. Industry will continue to refine the discharge volumes and will provide revisions, as necessary, to EPA.

Table 7 – Discharge Volume Estimate for Sampled Platforms

Platform	Discharge Volume Reported on OOC Hypoxia Registry Website or Updated in July 2005 (bbl/day)
EC 46B	4,200
EC 47JP	610
EC 49B	63
EI 107A	1,600
EI 128A-JC	2,050
EI 172A	67
EI 175B	1,445
EI 184A	5,591
EI 50-1	267
EI 57A	2,250
EI 74A	190
EI 95F	1,410
GI 19#3	63,828
HI 37A	50
HI 39A	100
HI 46A	67
SM 238-190	690
SM 23G	700
SM 268A	10,500
SM 33D	720
SM 40 JA	8
SS 108D	9,600
SS 157A	1,040
SS 169C	3,037
SS 182C	4,643
SS 182E	6,280
SS 189A	1,047
SS 191 B	1,700
SS 58A	1,927
ST 148E	1,311
ST 161A	68
ST 164C	1,355
ST 34A	4,497
VR 164A	245
VR 22B	150
VR119D	7,436
WC 102G	1,407
WC 110A	213
WC 130A	401
WC 168A	35

Platform	Discharge Volume Reported on OOC Hypoxia Registry Website or Updated in July 2005 (bbl/day)
WC 170A	1,300
WC 173K	40
WC 215A	1,290
WC 237A	3
WC 53A	292
WC 65JA	1,509
WC 71D	135
WD 45A	2,984
WD 73A	20,159
WD 89A	5,000
Total	175,510

An accurate estimate of the discharge volume is important for the hypoxic zone study because the primary impact of oxygen-demanding materials is the total mass loading to a water body rather than the specific concentration. Mass loading is determined by multiplying concentration, flow, and a conversion factor to make the units match. For example, assume 300 bbl/day flow and a concentration of BOD of 500 mg/L. The loading is:

$$500 \text{ mg/L} \times 159 \text{ L/bbl} \times 300 \text{ bbl/day} \times 1 \text{ lb}/454{,}000 \text{ mg} = 52.5 \text{ lb/day of BOD}$$

Flow is directly proportional to mass loading – if the flow estimate is too high by 30 percent, the mass loading will be overestimated by 30 percent. Modelers face a challenge to select the most appropriate volume estimates when estimating the impacts of produced water discharges to the hypoxic zone.

<u>Type of Hydrocarbon Produced</u>

Produced water volume and parameter concentrations may have some relationship to the type of hydrocarbon produced from the wells that contribute produced water to a discharge. The operators gave a general hydrocarbon status (mostly oil, mostly gas, or both oil and gas) for each platform. This is a qualitative estimate without any specific percentage cutoffs. The hydrocarbon status is shown in Table 8. Only 6 platforms reported primarily oil production and 20 reported primarily gas production. The remaining 24 platforms reported both types of hydrocarbon.

Table 8 – Type of Hydrocarbon Produced at Sampled Platforms

Platform	Primary Type of Hydrocarbon		Platform	Primary Type of Hydrocarbon
EC 46B	Both		EI 50-1	Gas
EC 47JP	Both		EI 74A	Gas
EI 107A	Both		HI 37A	Gas
EI 128A-JC	Both		HI 39A	Gas
EI 172A	Both		HI 46A	Gas
EI 175B	Both		SM 238-190	Gas
EI 57A	Both		SM 23G	Gas
EI 95F	Both		SM 268A	Gas
SM 33D	Both		ST 148E	Gas
SS 108D	Both		ST 161A	Gas
SS 157A	Both		ST 164C	Gas
SS 169C	Both		VR 22B	Gas
SS 182C	Both		WC 102G	Gas
SS 182E	Both		WC 110A	Gas
SS 189A	Both		WC 130A	Gas
SS 58A	Both		WC 173K	Gas
ST 34A	Both		WC 215A	Gas
VR 164A	Both		WC 53A	Gas
VR119D	Both		WC 71D	Gas
WC 168A	Both		EI 184A	Oil
WC 170A	Both		GI 19#3	Oil
WC 237A	Both		SM 40 JA	Oil
WD 73A	Both		SS 191 B	Oil
WD 89A	Both		WC 65JA	Oil
EC 49B	Gas		WD 45A	Oil

Chapter 4 – Sampling Results

This chapter provides a summary of the analytical results from sampling the 50 platforms that are part of the study. A complete set of results is found in Appendix D. Various excerpts and analyses of the full data set are presented here.

Statistical Summary of Data

Table 9 shows some basic statistics for all of the measured parameters. The mean and median give an estimate of the "average" of the data set, and the maximum and minimum show the extremes. The standard deviation (SD) shows the variability in the data set. The mean + 3 SD statistic gives a value slightly higher than the 99th percentile of the data set. The count is the number of data points considered for the particular parameter. The dissolved and particulate BOD and TOC were run on 8 or 9 (about 10 percent) of the samples. To avoid over-weighting the platforms that were sampled three times, the average of the three values[1] was used to represent the platform when calculating statistics.

Table 9 – Statistical Summary of Data

Parameter	Mean	Median	Maximum	Minimum	Standard Deviation	Mean + 3StDev	No. of Platforms
BOD, mg/L	957	583	11,108	80	1,656	5,924	50
Dissolved BOD, mg/L	498	432	1,128	132	297	1,389	9
Suspended BOD, mg/L	76	57	146	16	45	213	9
TOC, mg/L	564	261	4,880	26	987	3,524	50
Dissolved TOC, mg/L	216	147	620	67	184	769	8
Suspended TOC, mg/L	32	13	127	5	41	156	8
Nitrate, mg/L	2.15	1.15	15.80	0.60	3.04	11.26	50
Nitrite, mg/L	0.05	0.05	0.06	0.05	0.00	0.05	50
Ammonia, mg/L	74	74	246	14	49	221	50
TKN, mg/L	83	81	216	17	49	232	50
Orthophosphate, mg/L	0.43	0.14	6.60	0.10	1.05	3.56	50
Total phosphorus, mg/L	0.71	0.28	7.90	0.10	1.35	4.77	50
Conductivity, μmhos/cm	87,452	86,480	165,000	360	44,706	221,572	50
Salinity, ppt	100	84	251	0	68	304	50
Temperature, ^{o}C [a]	38	32	80	20	14	79	50
pH, SU	6.29	6.50	7.25	1.77	0.88[b]	8.94[b]	50

[a] The temperatures were measured in the field by personnel on the platforms. Although temperature should have been reported as ^{o}C, it is likely that some of the values were actually ^{o}F. Therefore, the statistics may not be representative.
[b] pH is measured on a logarithmic scale, so mean and SD values may not be representative.

[1] One of the three-time sampled platforms stopped producing water after the second sample, so only two data values are averaged to represent this platform. Another platform exhibited so much variability after three samples that the project protocol called for additional samples.

Temporal Variability

The results of the sampling of the 16 platforms that were sampled on more than one date show that concentrations do vary. The procedure approved by EPA for this project for determining acceptable variability among samples at the same platform looks only at BOD results. The procedure uses an acceptability criterion of CV <0.6. Fifteen of the sixteen platforms have CVs ranging from 0.10 to 0.46; these all demonstrate acceptable temporal variability. The sixteenth platform had a CV of 0.69 after three samples. Following a fourth sample, the CV increased to 0.94. At this point, the company was instructed to collect a fifth and sixth sample. Those results mirrored the earlier results in their inconsistency – one was high and the other much lower. The CV for all six samples is 1.08. Apparently this platform has a variable BOD concentration in its produced water discharge.

Although no CVs were calculated for parameters other than BOD, those parameters showed varying degree of temporal variability, too. Some platforms showed a great deal of consistency among the three samples. Others had two of the three samples at similar levels and the third sample at a somewhat different level.

The graphs presented in this chapter do not display the individual data points for each sample at the platforms sampled more than once. To avoid overweighting them, each platform is presented as an average of all samples collected at that location. This allows easy comparison of the spatial (or platform-to-platform) variability. To examine the temporal variability, readers must look at the individual sample results in Appendix D.

Consideration of Outliers

Outliers are data points that are substantially higher or lower than the rest of the data in a set. In data sets with high outlier values, the mean may be distorted by the outliers, and the median may be a better estimate of the "representative" value. In this data set, the mean and median were examined for each parameter. Where the two values are very different, the raw data were checked to see if the discrepancy was caused by one or a few outliers. Among the target parameters for this study (the oxygen-demanding substances), those that showed more than minimal discrepancy between mean and median (mean at least 1.5 times as high as median) are BOD, TOC, nitrate, orthophosphate, and total phosphorus. Each of these is discussed below.

BOD: Figure 5 shows the BOD values from all platforms in bar chart format, listed alphabetically by lease. Each bar represents a different platform; where more than one sample was collected at a platform, the bar represents the average of the samples. Two values clearly stand out from the rest of the data here. The highest value is 11,108 mg/L and the second highest is 5,378 mg/L. The remaining values are all less than 2,000 mg/L.

Table 10 shows the effect on BOD statistics if first one and then both of these outliers are removed from the data set. As the outliers are removed from the data set, the mean decreases by 32 percent and the mean and median become more similar. The SD decreases by 76 percent.

Figure 5 – Plot of BOD Results from All Platforms (values shown in mg/L)

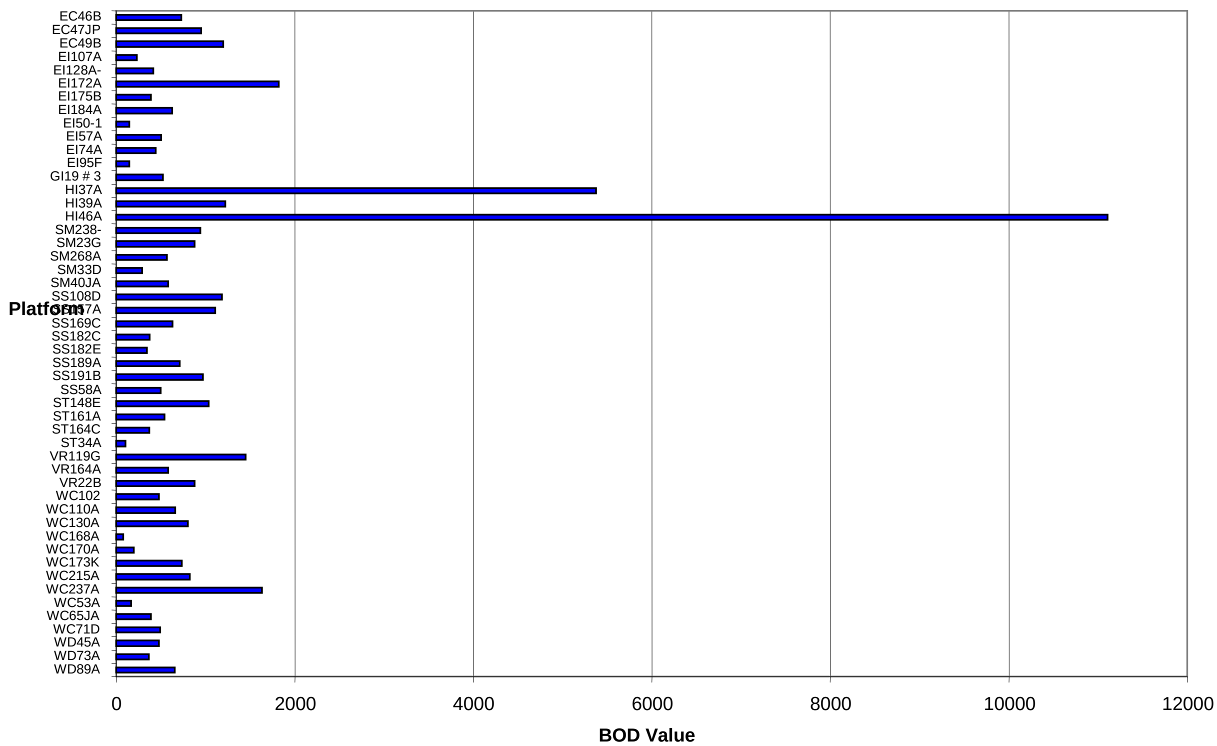


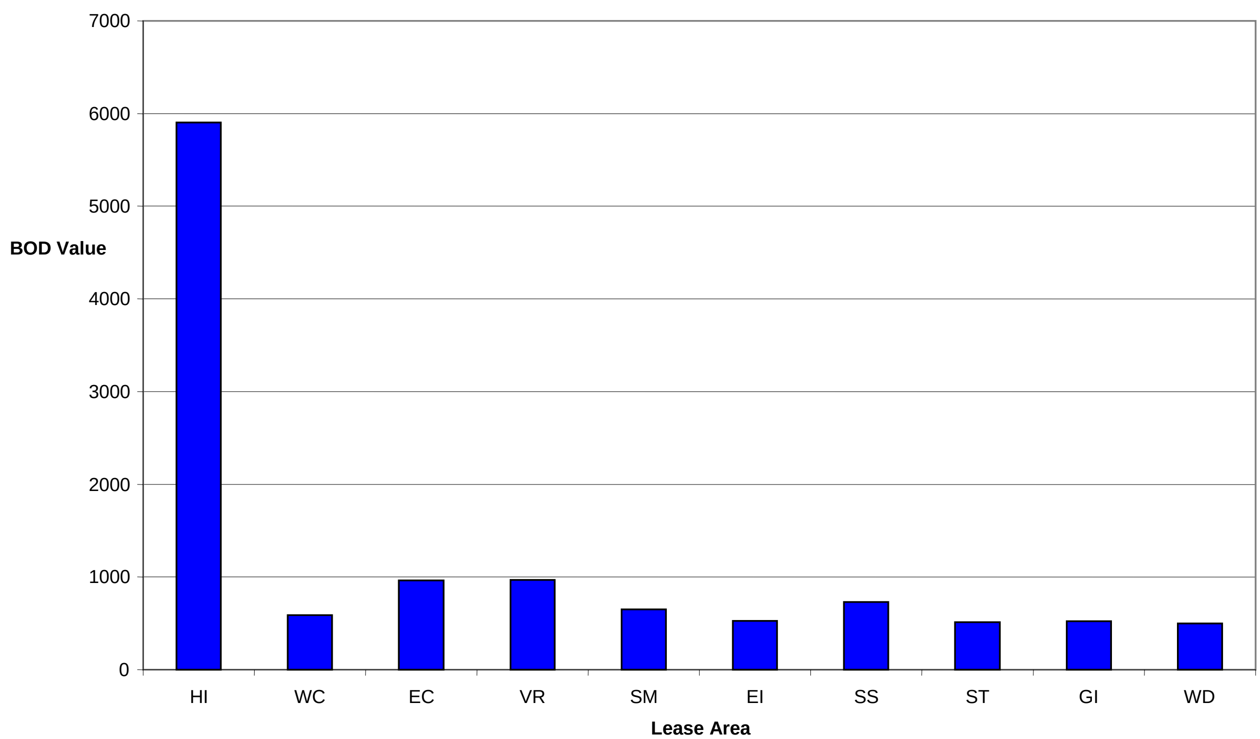
Table 10 – Change in Statistical Properties after Removing BOD Outliers

Parameter	Mean	Median	Maximum	Minimum	SD	Mean + 3 SD	No. of Platforms
All BOD data, mg/L	957	583	11,108	80	1,656	5,924	50
All BOD data except highest outlier, mg/L	750	582	5,378	80	780	3,089	49
All BOD data except two highest outliers, mg/L	654	576	1,821	80	394	1,837	48

Outliers should not automatically be dropped from data sets without a clear understanding of why they differ from the rest of the data set. In this instance, the two BOD outlier data points were measured at platforms in the HI (High Island) lease area, which is the westernmost lease area included in the study.

Figure 6 shows a plot of average BOD by lease area, with lease areas portrayed in sequence from west to east. The average BOD for HI is nearly 6,000 mg/L. No other extremely high values were reported in any different lease area, and none of the other average BOD values exceeds 1,000 mg/L. All of the HI platforms sampled in this program, as well as all other HI platforms listed on the OOC hypoxia registry website, are primarily gas producers. The lighter hydrocarbons in gas may be more soluble and more readily detectable under the BOD test.

Figure 6 – BOD Values by Lease Area (values shown in mg/L)



The OOC hypoxia registry website contains 287 platforms located throughout the hypoxic zone. Only 10 of the 296 registered platforms (about 3 percent) are located in the High Island lease area. There is no reason to believe the two outliers are erroneous data points (i.e., incorrectly collected sample, bad lab analysis). Nevertheless, they are not typical of most of the area within the hypoxic zone and should probably be treated separately when water quality models are run.

TOC: Figure 7 shows the TOC values from all platforms in bar chart format. Four values clearly stand out from the rest of the data here. Two of the values exceed 4,000 mg/L and the other two exceed 2,000 mg/L. The remaining values are all less than 1,000 mg/L. The two platforms that had high BOD are part of this group of four high-TOC platforms. They are the second and third highest TOC values (4,700 mg/L and 2,440 mg/L). The highest (4,880 mg/L) and fourth highest (2,990 mg/L) TOC values are found at platforms that were not outliers for BOD.

Figure 7 – Plot of TOC Results from All Platforms (values shown in mg/L)

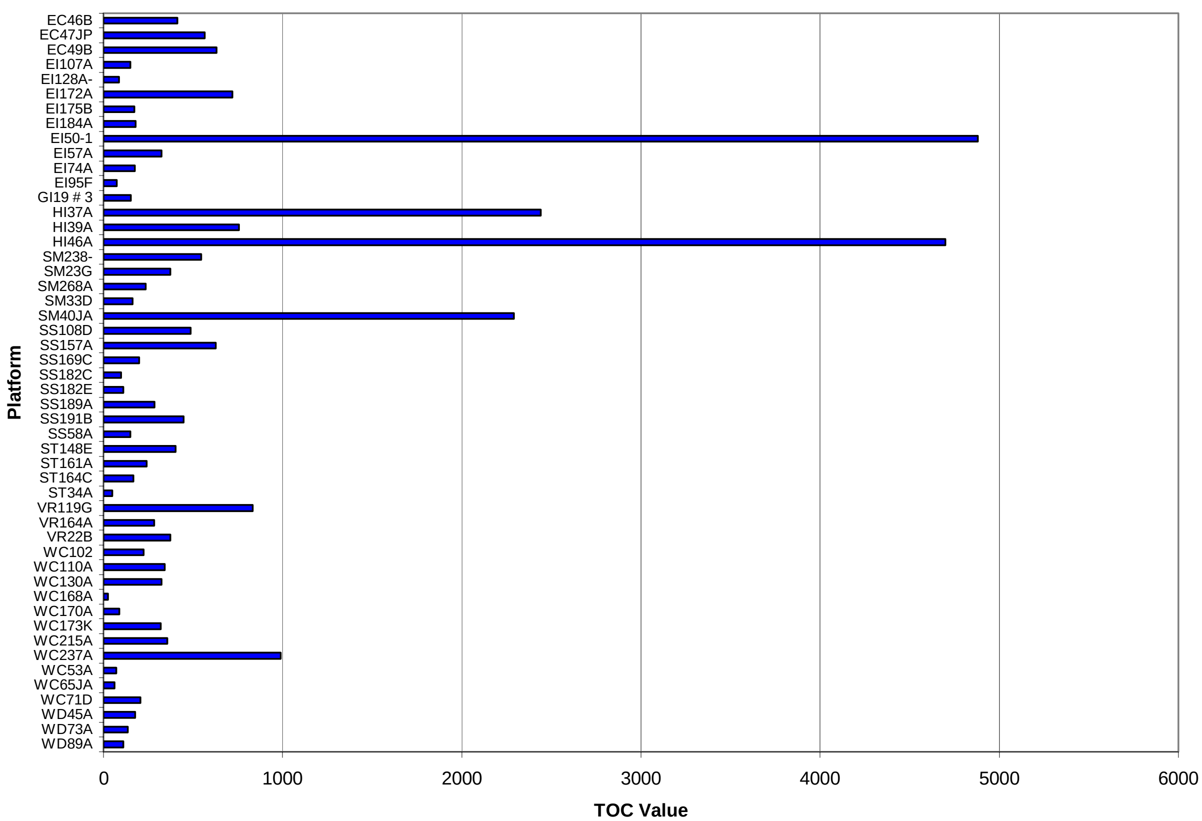


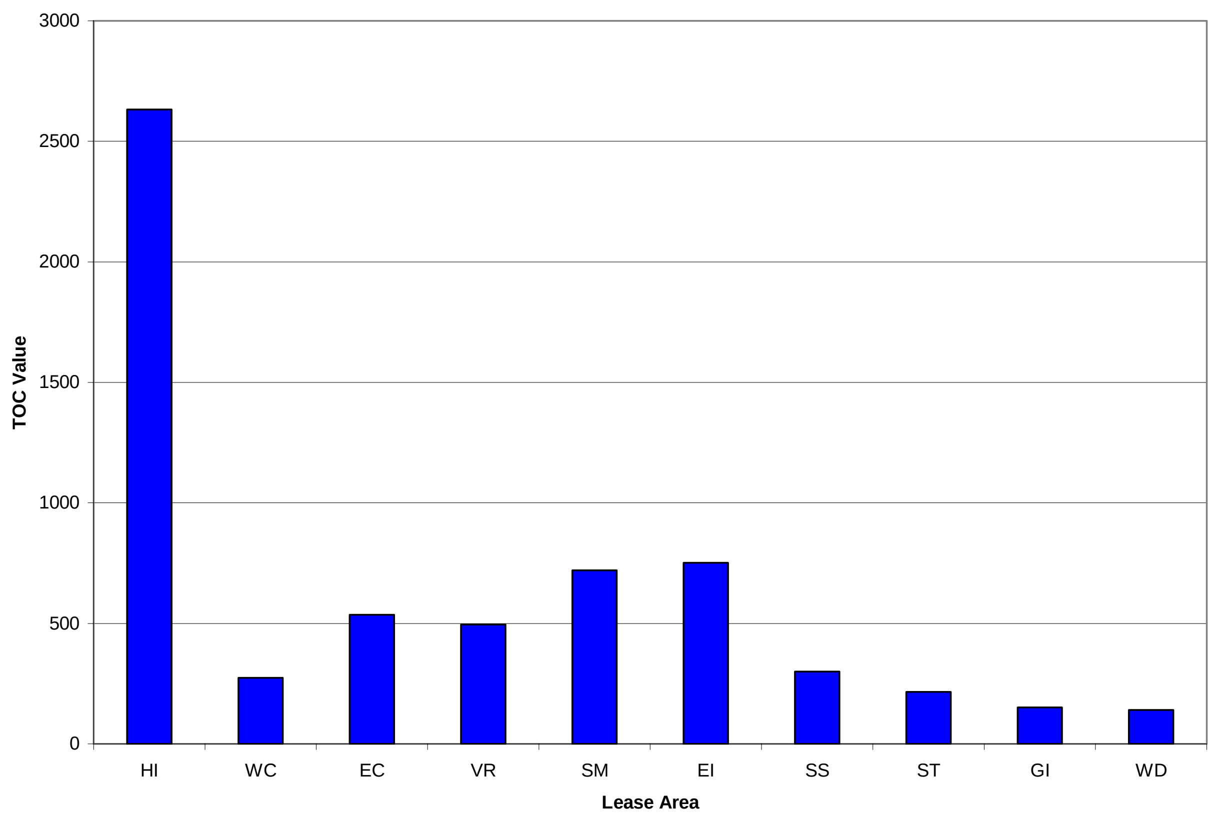
Table 11 shows the effect on TOC statistics if the two highest and then the four highest outliers are removed from the data set. As the outliers are removed from the data set, the mean decreases by 46 percent,and the mean and median become more similar. The SD decreases by 77 percent.

Table 11 – Change in Statistical Properties after Removing TOC Outliers

Parameter	Mean	Median	Maximum	Minimum	SD	Mean + 3 SD	No. of Platforms
All TOC data, mg/L	563	238	4,880	26	987	3,524	50
All TOC data except two highest outliers, mg/L	388	238	2,440	26	472	1,805	48
All BOD data except four highest outliers, mg/L	302	230	990	26	227	982	46

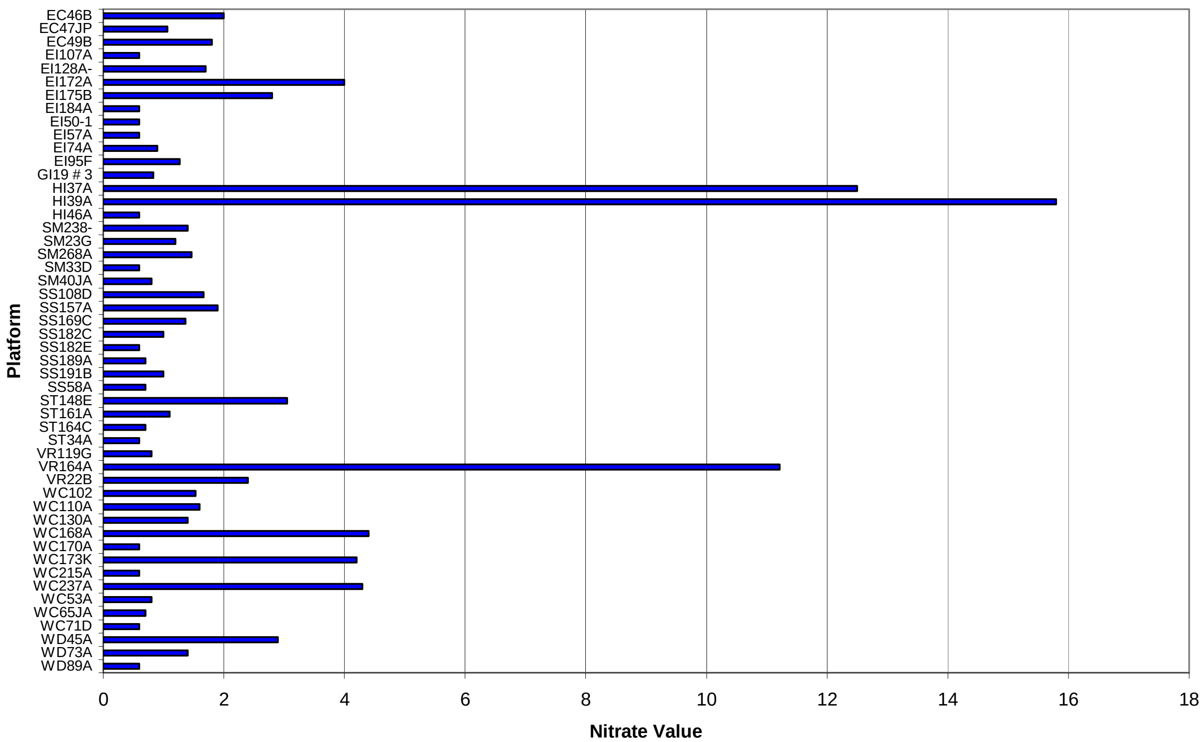
Figure 8 shows a plot of average TOC by lease area, with lease areas portrayed in sequence from west to east. High Island area shows a high concentration of TOC, but there is more variation in the other blocks than was seen for BOD in Figure 6. TOC concentration appears to decrease to the eastern edge of the hypoxic zone.

Figure 8 – TOC Values by Lease Area (values shown in mg/L)



Nitrate: Figure 9 shows the nitrate values from all platforms in bar chart format. Three values clearly stand out from the rest of the data here. They are 15.8 mg/L, 12.5 mg/L, and 11.2 mg/L. The remaining values all are less than 5 mg/l.

Figure 9 – Plot of Nitrate Results from All Platforms (values shown in mg/L)



Although not shown in Figure 9 because only platform averages are reported for those platforms sampled more than once, the highest individual result was at VR 164A, the platform sampled six times. That value was 57.5 mg/L. The other five results from that platform were much lower (0.6 mg/L, 0.6 mg/L, 0.7 mg/L, 0.9 mg/l, and 7.0 mg/L). The average for the platform is still high enough to be one of the outlier values.

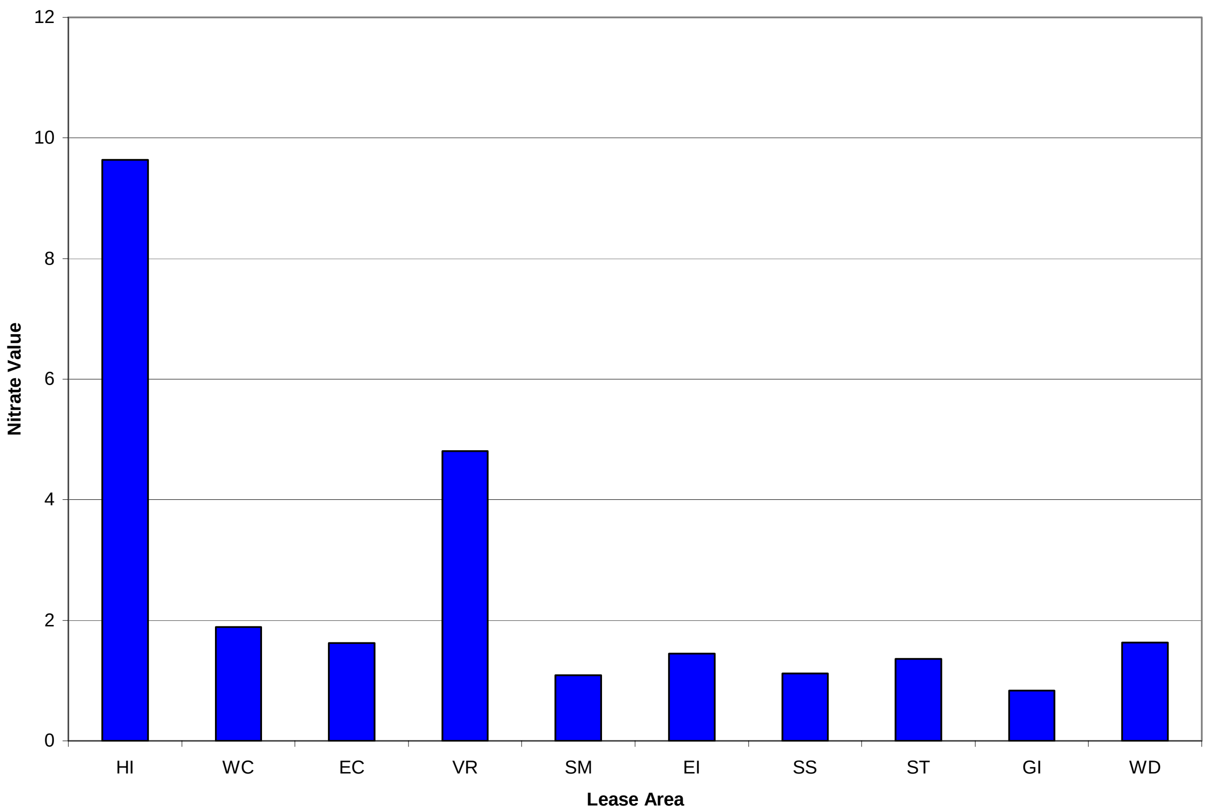
Table 12 shows the effect on nitrate statistics if these three outliers are removed from the data set. As the outliers are removed from the data set, the mean decreases by 36 percent and the mean and median become more similar. The SD decreases by 63 percent.

Table 12 – Change in Statistical Properties after Removing Nitrate Outliers

Parameter	Mean	Median	Maximum	Minimum	SD	Mean + 3 SD	No. of Platforms
All NO_3 data, mg/L	2.2	1.2	15.8	0.6	3.0	11.3	50
All NO_3 data except three highest outliers, mg/L	1.4	1.1	4.4	0.6	1.1	4.7	50

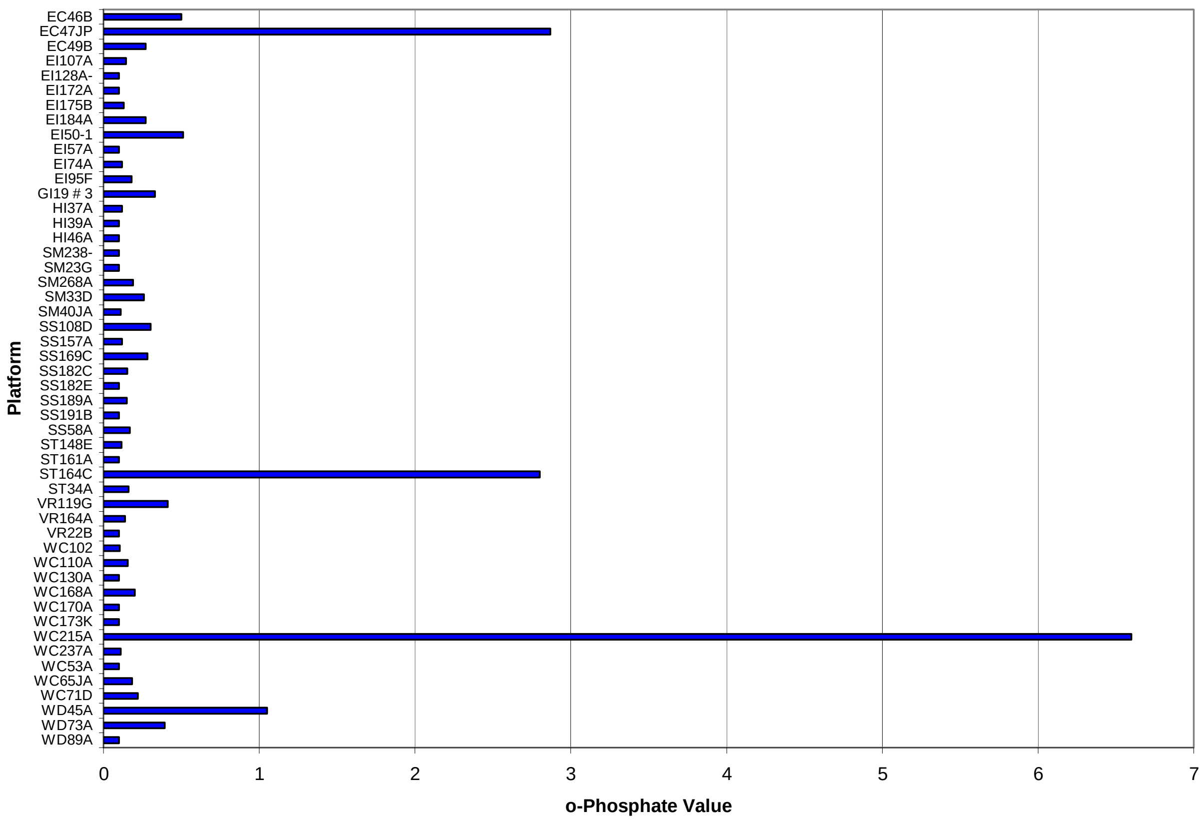
Figure 10 shows a plot of average nitrate by lease area, with lease areas portrayed in sequence from west to east. The High Island area shows a high concentration of nitrate, with a secondary peak showing for Vermillion. The other lease areas have relatively consistent levels of nitrate.

Figure 10 – Nitrate Values by Lease Area (values shown in mg/L)



Orthophosphate: Figure 11 shows the orthophosphate values from all platforms in bar chart format. Three values clearly stand out from the rest of the data here. The highest value is 6.6 mg/L, and the second and third highest are both about 2.8 mg/L. The remaining values all are less than 1.1 mg/L. All results from individual platforms are averaged, and then all platforms in a lease area are averaged again. This potentially can disguise the impact of a single high sample result.

Figure 11 – Plot of Orthophosphate Results from All Platforms (values shown in mg/L)



Although not shown in Figure 11 because only platform averages are reported for those platforms sampled more than once, the highest individual result was at a three-time sampled platform. That value was 8.1 mg/L. The other two results from that platform were much lower (0.16 mg/L and 0.35 mg/L). The average for the platform is still high enough to be one of the outlier values.

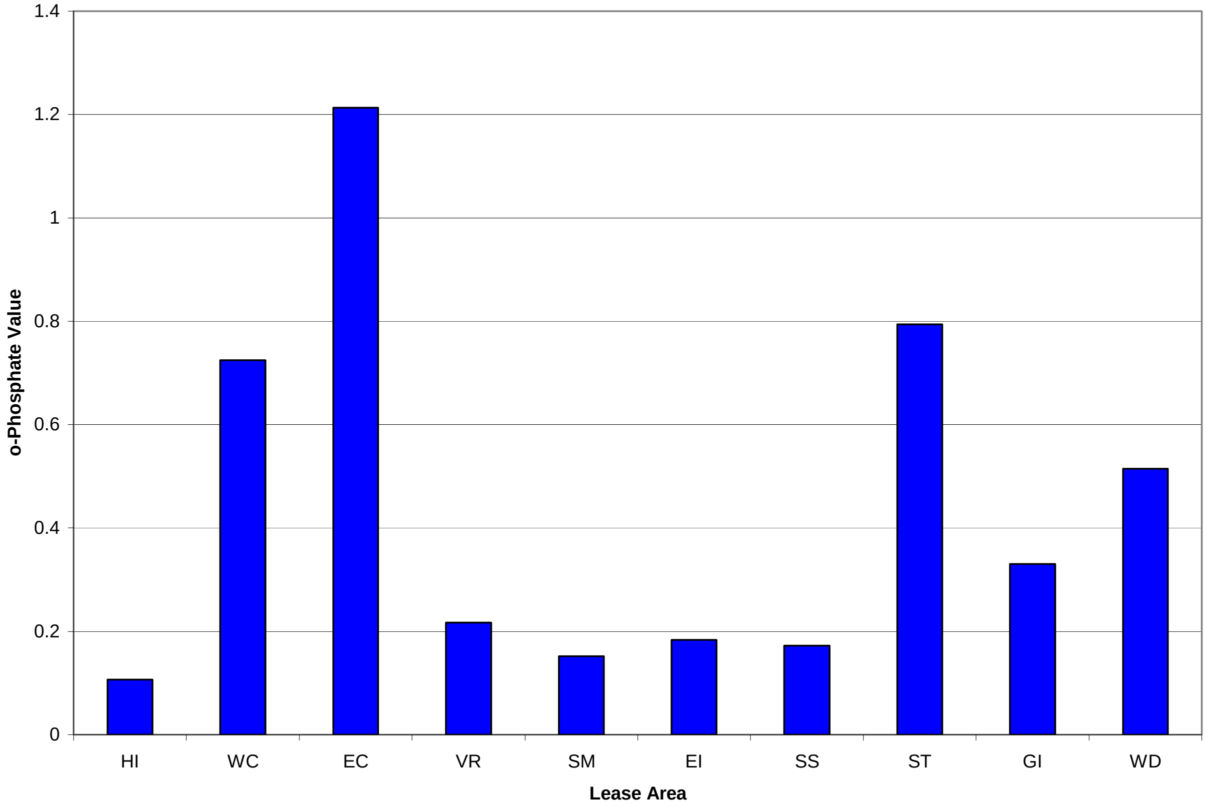
Table 13 shows the effect on orthophosphate statistics if the highest and then the three highest outliers are removed from the data set. As the outliers are removed from the data set, the mean decreases by 56 percent and the mean and median become more similar. The SD decreases by 84 percent.

Table 13 – Change in Statistical Properties after Removing Orthophosphate Outliers

Parameter	Mean	Median	Maximum	Minimum	SD	Mean + 3 SD	No. of Platforms
All ortho-P data, mg/L	0.4	0.1	6.6	0.1	1.1	3.6	50
All ortho-P data except highest outlier, mg/L	0.3	0.1	2.9	0.1	0.6	2.0	49
All ortho-P data except three highest outliers, mg/L	0.2	0.1	1.1	0.1	0.2	0.7	47

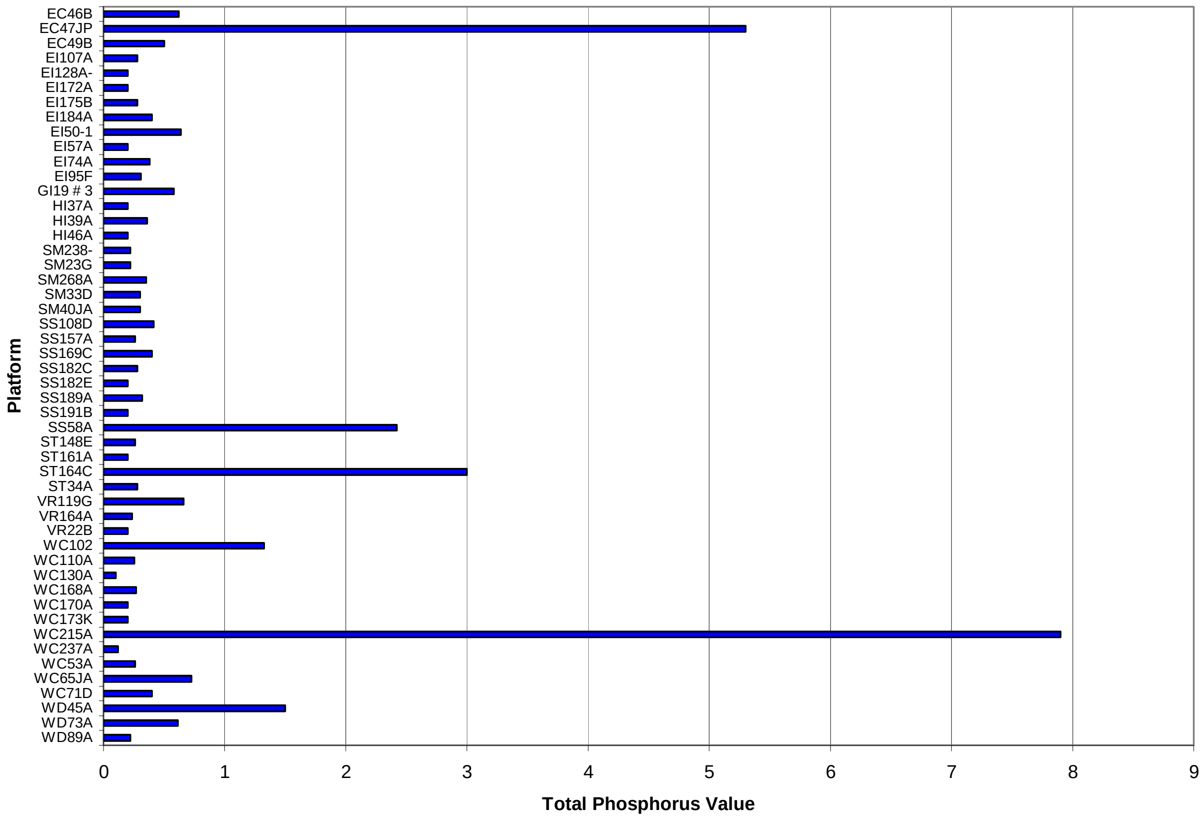
Figure 12 shows a plot of average orthophosphate by lease area, with lease areas portrayed in sequence from west to east. Unlike the previous geographic plots, the High Island area does not have a substantially higher average concentration. There is much more variation in the other blocks, with peaks in East Cameron, South Timbalier, West Cameron, and West Delta. All results from individual platforms are averaged, and then all platforms in a lease area are averaged again. This potentially can disguise the impact of a single high sample result.

Figure 12 – Orthophosphate Values by Lease Area (values shown in mg/L)



Total Phosphorus: Figure 13 shows the total phosphorus values from all platforms in bar chart format. Unlike the other parameters that were previously discussed, this distribution is more complicated. Most of the data points are less than 1.0 mg/L, but six platforms have values higher than 2.0 mg/L, and four platforms have values equal to or higher than 3.0 mg/L.

Figure 13 – Plot of Total Phosphorus Results from All Platforms (values shown in mg/L)



The highest value for a platform is 7.9 mg/L, although one value at a platform sampled three times was measured at 10.6 mg/L. However, when averaged with the other two samples, the mean at that platform is 5.3 mg/L.

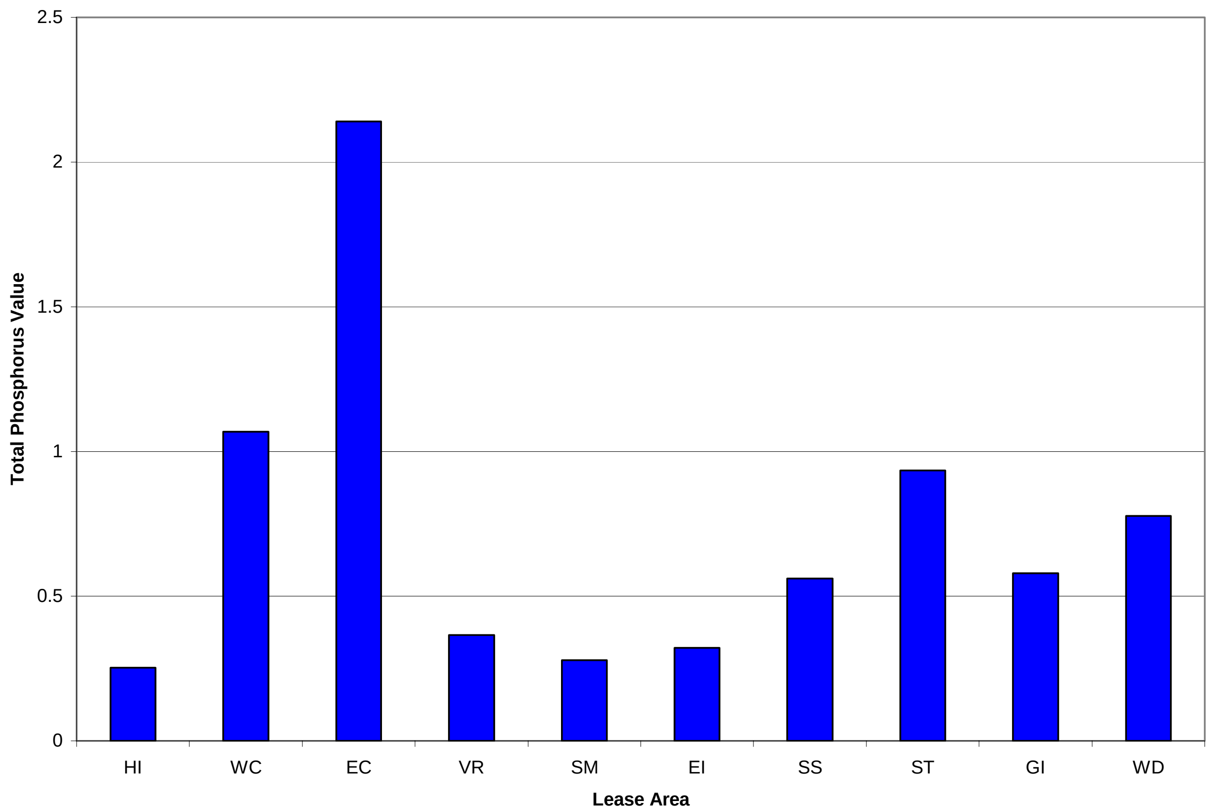
Table 14 shows the effect on total phosphorus statistics if the two highest and then the four highest outliers are removed from the data set. As the outliers are removed from the data set, the mean decreases by 48 percent and the mean and median become more similar. The SD decreases by 80 percent.

Table 14 – Change in Statistical Properties after Removing Total Phosphorus Outliers

Parameter	Mean	Median	Maximum	Minimum	SD	Mean + 3 SD	No. of Platforms
All total-P data, mg/L	0.71	0.28	7.90	0.10	1.35	4.77	50
All total-P data except two highest outlier, mg/L	0.46	0.28	3.00	0.10	0.55	2.10	48
All total-P data except four highest outliers, mg/L	0.37	0.28	1.50	0.10	0.27	1.18	46

Figure 14 shows a plot of average total phosphorus by lease area, with lease areas portrayed in sequence from west to east. East Cameron has the highest total phosphorus, followed by West Cameron, South Timbalier, and West Delta.

Figure 14 – Total Phosphorus Values by Lease Area (values shown in mg/L)



Associations between Parameters

Some of the parameters sampled in this study are expected to exhibit an association with other parameters. For example, TKN is the sum of ammonia and organic nitrogen. Therefore, TKN and ammonia may be closely related unless organic nitrogen concentrations are extremely high, which is not the case for produced water. Linear regression correlations between selected pairs of parameters were calculated and are displayed in Table 15. Although many different comparisons could be made here, several examples are shown as illustrations of possible associations. A positive correlation coefficient indicates a direct association (e.g., as parameter A increases, so does parameter B). A negative correlation coefficient indicates that as parameter A increases, parameter B decreases. Correlation coefficients range from 0 to1, or from 0 to –1 for negative correlations. A correlation coefficient near to 1 or –1 indicates a strong association between the two parameters, while a correlation coefficient near 0 indicates a weak association. The number of samples is considered when evaluating the significance of the association.

Table 15 – Linear Regression Correlations between Parameters

Parameter A	Parameter B	Correlation Coefficient	No. of Samples
BOD	Dissolved BOD	0.98	9
TOC	Dissolved TOC	0.96	8
BOD	TOC	0.67	50
Ammonia	TKN	0.97	50
Ammonia	Nitrate	–0.32	50
Ammonia	Nitrite	–0.11	50
Orthophosphate	Total phosphorous	0.95	50
Conductivity	Salinity	0.97	50

The association between BOD and dissolved BOD is very strong, as is the association between TOC and dissolved TOC. This reflects the large percentage of both BOD (97 percent) and TOC (89 percent) that are in the dissolved form. The association between BOD and TOC is not as strong as some of the other correlations.

For the nutrients, ammonia correlates very well with TKN (i.e., increases in ammonia track closely to increases in TKN). Since ammonia makes up about 95 percent of the TKN, this is not surprising. Ammonia does not correlate well with nitrate or nitrite. The correlation coefficients for both are low. The association between these parameters is a negative correlation. Orthophosphate correlates very well with total phosphorus.

The high correlation between conductivity and salinity is not surprising, because they are both measuring similar properties.

<u>Relationship between Type of Hydrocarbon Produced and Concentrations</u>

One of the factors used to select the platforms that were tested three times is the type of hydrocarbon produced by a platform. Table 8 shows the primary hydrocarbon production for each of the 50 platforms in the study. Table 16 provides average concentrations of the oxygen-demanding and nutrient parameters for the platforms in each of three production categories (mostly oil, mostly gas, and a mix of both oil and gas). As noted previously, produced water from gas production often contains a higher proportion of lighter hydrocarbons that are more soluble. This is demonstrated by comparing the average BOD and TOC concentrations from the mostly-oil and mostly-gas platforms. The mostly-gas platforms have considerably higher average BOD and TOC values. The data indicate that nitrate, orthophosphate, and total phosphorus are higher in the mostly-gas platforms, whereas ammonia and TKN are higher in the mostly-oil platforms. The average concentrations for the platforms having both types of production are not consistently above, below, or in between the mostly-oil and mostly-gas platform averages.

Table 16 – Average Concentrations Displayed by Type of Hydrocarbon Produced from a Platform

	Average Concentration (mg/L) for All Platforms in a Hydrocarbon Production Category		
Parameter	**6 Platforms Producing Mostly Oil**	**20 Platforms Producing Mostly Gas**	**24 Platforms Producing Both Oil and Gas**
BOD	595	1,444	642
TOC	551	888	297
Nitrate	1.14	2.71	1.94
Nitrite	0.05	0.05	0.05
Ammonia	92	57	85
TKN	111	65	92
Ortho-P	0.34	0.61	0.30
Total-P	0.62	0.86	0.61

Chapter 5 – Estimation of Mass Loading

A primary goal of this study is to estimate the mass loading of each of the oxygen-demanding pollutants from the 50 platforms sampled in the study. As noted in Chapter 3, mass loading is calculated by multiplying concentrations (reported in Chapter 4 and Appendix D) by the discharge volume (reported in Chapter 3) and then by a conversion factor to allow units to match.

Uncertainty

Neither concentration nor discharge volume is a fixed quantity, nor is there necessarily a relationship between them. Both fluctuate over time, so it is difficult to provide a single-number estimate for either factor or for the load. The analytical data for the measured parameters should be reasonably accurate and exhibit a low degree of uncertainty. The QA/QC procedures implemented for this study provide confidence in the fundamental accuracy of the data. The variability within any particular parameter differs from platform to platform and over time, as indicated by the platforms sampled more than once. The variability is not consistent between parameters, either. While the project's limitations on timing and number of samples precluded long-term sampling, a significant fraction of the total volume of produced water discharged to the hypoxic zone was evaluated. Regardless, considering the wide range of geological conditions from which the produced waters are drawn, a certain degree of variability is inevitable.

One important issue related to concentration is how values reported as "less than" (below the method detection limit, or MDL) are treated. Some of the analytical results for nitrate, nitrite, orthophosphate, and total phosphorus are reported that way by the analytical laboratory. This means that the actual concentration for those analyses falls somewhere between zero and the "less than" value reported. For example, many nitrite values are reported as <0.05 mg/L. When calculating loads, these values can be treated as equal to 0.05 mg/L, as zero, or as some value in between.

Perhaps the largest source of variability and uncertainty relates to having accurate discharge volume values. Table 7 shows the data entered by operators to the OOC hypoxic zone registry during the winter of 2004-2005. More recent and accurate average data were provided in June and July of 2005 for a few platforms; the updated values were substituted into Table 7. It is difficult to characterize the variable volume of produced water that is discharged over time (see Table 6 for examples) by a single value. Nevertheless, this is the only complete set of volume data available at this time.

Estimation Methodology

For concentration, the average value for each platform is used. Any "less than" values are treated as being equal to the value following the "less than" sign (e.g., the nitrite values mentioned earlier would be treated as equal to 0.05 mg/L). This overestimates the true concentration for those values, and, as such, is a conservative approach. For discharge volume, the volume figures from Table 7 are used.

Loading Estimates

Tables 17 to 20 show the discharge volume for each platform followed by concentration and loading for the oxygen-demanding parameters.

Table 17 – Loading Estimates for BOD and TOC

Platform	Discharge Volume (bbl/day)	BOD Concentration (mg/L)	BOD Loading (lb/day)	TOC Concentration (mg/L)	TOC Loading (lb/day)
EC 46B	4,200	732	1,080	412	606
EC 47JP	610	954	204	565	121
EC 49B	63	1,200	26	630	14
EI 107A	1,600	234	131	150	84
EI 128A-JC	2,050	415	298	86	62
EI 172A	67	1,821	43	720	17
EI 175B	1,445	392	198	172	87
EI 184A	5,591	628	1,230	178	349
EI 50-1	267	147	14	4,880	456
EI 57A	2,250	503	396	325	256
EI 74A	190	442	29	174	12
EI 95F	1,410	148	73	74	37
GI 19#3	63,828	521	11,600	151	3,380
HI 37A	50	5,378	94	2,440	43
HI 39A	100	1,224	43	755	26
HI 46A	67	11,108	261	4,700	110
SM 238-190	690	940	227	545	132
SM 23G	700	876	215	374	92
SM 268A	10,500	569	2,090	236	868
SM 33D	720	289	73	162	41
SM 40 JA	8	582	2	2,290	6
SS 108D	9,600	1,186	3,990	487	1,640
SS 157A	1,040	1,108	404	625	228
SS 169C	3,037	632	672	199	212
SS 182C	4,643	376	612	99	161
SS 182E	6,280	344	757	111	244
SS 189A	1,047	711	261	286	105
SS 191 B	1,700	974	580	448	267
SS 58A	1,927	499	337	149	101
ST 148E	1,311	1,038	477	403	185
ST 161A	68	543	13	240	6
ST 164C	1,355	372	177	168	80
ST 34A	4,497	103	162	50	78
VR 164A	245	583	50	283	24
VR 22B	150	879	46	374	20
VR 119D	7,436	1,448	3,770	832	2,170
WC 102G	1,407	479	236	224	110
WC 110A	213	663	49	341	25

Platform	Discharge Volume (bbl/day)	BOD Concentration (mg/L)	BOD Loading (lb/day)	TOC Concentration (mg/L)	TOC Loading (lb/day)
WC 130A	401	804	113	324	46
WC 168A	35	80	1	26	0
WC 170A	1,300	198	90	89	40
WC 173K	40	736	10	320	4
WC 215A	1,290	826	373	356	161
WC 237A	3	1,632	2	990	1
WC 53A	292	167	17	72	7
WC 65JA	1,509	389	206	62	33
WC 71D	135	494	23	206	10
WD 45A	2,984	477	498	176	184
WD 73A	20,159	365	2,580	134	948
WD 89A	5,000	654	1,150	110	193
Total	175,510		36,000		14,100

Table 18 – Loading Estimates for Nitrate and Nitrite

Platform	Discharge Volume (bbl/day)	Nitrate Concentration (mg/L)	Nitrate Loading (lb/day)	Nitrite Concentration (mg/L)	Nitrite Loading (lb/day)
EC 46B	4,200	2.00	2.94	0.05	0.07
EC 47JP	610	1.07	0.23	0.05	0.01
EC 49B	63	1.80	0.04	0.05	0.00
EI 107A	1,600	0.60	0.34	0.05	0.03
EI 128A-JC	2,050	1.70	1.22	0.05	0.04
EI 172A	67	4.00	0.09	0.05	0.00
EI 175B	1,445	2.80	1.42	0.05	0.03
EI 184A	5,591	0.60	1.17	0.05	0.10
EI 50-1	267	0.60	0.06	0.05	0.00
EI 57A	2,250	0.60	0.47	0.05	0.04
EI 74A	190	0.90	0.06	0.05	0.00
EI 95F	1,410	1.27	0.63	0.05	0.02
GI 19#3	63,828	0.83	18.6	0.05	1.12
HI 37A	50	12.50	0.22	0.05	0.00
HI 39A	100	15.80	0.55	0.05	0.00
HI 46A	67	0.60	0.01	0.05	0.00
SM 238-190	690	1.40	0.34	0.05	0.01
SM 23G	700	1.20	0.29	0.05	0.01
SM 268A	10,500	1.47	5.39	0.05	0.18
SM 33D	720	0.60	0.15	0.05	0.01
SM 40 JA	8	0.80	0.00	0.05	0.00
SS 108D	9,600	1.67	5.60	0.05	0.17
SS 157A	1,040	1.90	0.69	0.05	0.02
SS 169C	3,037	1.37	1.45	0.05	0.05
SS 182C	4,643	1.00	1.63	0.05	0.08

Platform	Discharge Volume (bbl/day)	Nitrate Concentration (mg/L)	Nitrate Loading (lb/day)	Nitrite Concentration (mg/L)	Nitrite Loading (lb/day)
SS 182E	6,280	0.60	1.32	0.05	0.11
SS 189A	1,047	0.70	0.26	0.05	0.02
SS 191 B	1,700	1.00	0.60	0.05	0.03
SS 58A	1,927	0.70	0.47	0.05	0.03
ST 148E	1,311	3.05	1.40	0.05	0.02
ST 161A	68	1.10	0.03	0.05	0.00
ST 164C	1,355	0.70	0.33	0.05	0.02
ST 34A	4,497	0.60	0.94	0.05	0.08
VR 164A	245	11.22	0.96	0.055	0.00
VR 22B	150	2.40	0.13	0.05	0.00
VR 119D	7,436	0.80	2.08	0.05	0.13
WC 102G	1,407	1.53	0.76	0.05	0.02
WC 110A	213	1.60	0.12	0.05	0.00
WC 130A	401	1.40	0.20	0.05	0.01
WC 168A	35	4.40	0.05	0.05	0.00
WC 170A	1,300	0.60	0.27	0.05	0.02
WC 173K	40	4.20	0.06	0.05	0.00
WC 215A	1,290	0.60	0.27	0.05	0.02
WC 237A	3	4.30	0.00	0.05	0.00
WC 53A	292	0.80	0.08	0.05	0.01
WC 65JA	1,509	0.70	0.37	0.05	0.03
WC 71D	135	0.60	0.03	0.05	0.00
WD 45A	2,984	2.90	3.03	0.05	0.05
WD 73A	20,159	1.40	9.88	0.05	0.35
WD 89A	5,000	0.60	1.05	0.05	0.09
Total	175,510		68.3		3.07

Table 19 – Loading Estimates for Ammonia and TKN

Platform	Discharge Volume (bbl/day)	Ammonia Concentration (mg/L)	Ammonia Loading (lb/day)	TKN Concentration (mg/L)	TKN Loading (lb/day)
EC 46B	4,200	115	169	122	179
EC 47JP	610	33	7	40	9
EC 49B	63	64	1	74	2
EI 107A	1,600	78	44	92	52
EI 128A-JC	2,050	21	15	24	17
EI 172A	67	34	1	39	1
EI 175B	1,445	35	18	37	19
EI 184A	5,591	40	78	67	132
EI 50-1	267	50	5	59	6
EI 57A	2,250	54	43	89	70
EI 74A	190	103	7	111	7
EI 95F	1,410	58	29	63	31

Platform	Discharge Volume (bbl/day)	Ammonia Concentration (mg/L)	Ammonia Loading (lb/day)	TKN Concentration (mg/L)	TKN Loading (lb/day)
GI 19#3	63,828	93	2,090	98	2,180
HI 37A	50	54	1	74	1
HI 39A	100	75	3	82	3
HI 46A	67	129	3	134	3
SM 238-190	690	86	21	106	26
SM 23G	700	51	13	46	11
SM 268A	10,500	121	445	128	471
SM 33D	720	160	40	168	42
SM 40 JA	8	48	0	50	0
SS 108D	9,600	38	127	36	122
SS 157A	1,040	59	21	64	23
SS 169C	3,037	102	108	111	118
SS 182C	4,643	100	163	110	179
SS 182E	6,280	104	229	109	240
SS 189A	1,047	16	6	17	6
SS 191 B	1,700	69	41	80	48
SS 58A	1,927	20	14	40	27
ST 148E	1,311	183	84	192	88
ST 161A	68	51	1	60	1
ST 164C	1,355	27	13	36	17
ST 34A	4,497	246	387	216	340
VR 164A	245	32	3	42	4
VR 22B	150	101	5	178	9
VR 119D	7,436	27	71	37	97
WC 102G	1,407	79	39	79	39
WC 110A	213	98	7	120	9
WC 130A	401	96	14	101	14
WC 168A	35	16	0	17	0
WC 170A	1,300	20	9	32	15
WC 173K	40	36	1	42	1
WC 215A	1,290	109	49	113	51
WC 237A	3	63	0	73	0
WC 53A	292	43	4	56	6
WC 65JA	1,509	140	74	154	81
WC 71D	135	30	1	37	2
WD 45A	2,984	81	84	84	88
WD 73A	20,159	22	158	31	216
WD 89A	5,000	15	26	20	35
Total	175,510		4,770		5,140

Table 20 – Loading Estimates for Orthophosphate and Total Phosphorus

Platform	Discharge Volume (bbl/day)	Orthophosphate Concentration (mg/L)	Orthophosphate Loading (lb/day)	Total P Concentration (mg/L)	Total P Loading (lb/day)
EC 46B	4,200	0.50	0.74	0.62	0.91
EC 47JP	610	2.87	0.61	5.30	1.13
EC 49B	63	0.27	0.01	0.50	0.01
EI 107A	1,600	0.15	0.08	0.28	0.16
EI 128A-JC	2,050	0.10	0.07	0.20	0.14
EI 172A	67	0.10	0.00	0.20	0.00
EI 175B	1,445	0.13	0.07	0.28	0.14
EI 184A	5,591	0.27	0.53	0.40	0.78
EI 50-1	267	0.51	0.05	0.64	0.06
EI 57A	2,250	0.10	0.08	0.20	0.16
EI 74A	190	0.12	0.01	0.38	0.03
EI 95F	1,410	0.18	0.09	0.31	0.15
GI 19#3	63,828	0.33	7.38	0.58	13.0
HI 37A	50	0.12	0.00	0.20	0.00
HI 39A	100	0.10	0.00	0.36	0.01
HI 46A	67	0.10	0.00	0.20	0.00
SM 238-190	690	0.10	0.02	0.22	0.05
SM 23G	700	0.10	0.02	0.22	0.05
SM 268A	10,500	0.19	0.70	0.35	1.30
SM 33D	720	0.26	0.07	0.30	0.08
SM 40 JA	8	0.11	0.00	0.30	0.00
SS 108D	9,600	0.30	1.02	0.41	1.39
SS 157A	1,040	0.12	0.04	0.26	0.09
SS 169C	3,037	0.28	0.30	0.40	0.43
SS 182C	4,643	0.15	0.25	0.28	0.46
SS 182E	6,280	0.10	0.22	0.20	0.44
SS 189A	1,047	0.15	0.06	0.32	0.12
SS 191 B	1,700	0.10	0.06	0.20	0.12
SS 58A	1,927	0.17	0.11	2.42	1.63
ST 148E	1,311	0.12	0.05	0.26	0.12
ST 161A	68	0.10	0.00	0.20	0.00
ST 164C	1,355	2.80	1.33	3.00	1.42
ST 34A	4,497	0.16	0.25	0.28	0.44
VR 164A	245	0.14	0.01	0.24	0.02
VR 22B	150	0.10	0.01	0.20	0.01
VR 119D	7,436	0.41	1.08	0.66	1.72
WC 102G	1,407	0.10	0.05	1.33	0.65
WC 110A	213	0.16	0.01	0.25	0.02
WC 130A	401	0.10	0.01	0.10	0.01
WC 168A	35	0.20	0.00	0.27	0.00
WC 170A	1,300	0.10	0.05	0.20	0.09
WC 173K	40	0.10	0.00	0.20	0.00
WC 215A	1,290	6.60	2.98	7.90	3.57
WC 237A	3	0.11	0.00	0.12	0.00

Platform	Discharge Volume (bbl/day)	Orthophosphate Concentration (mg/L)	Orthophosphate Loading (lb/day)	Total P Concentration (mg/L)	Total P Loading (lb/day)
WC 53A	292	0.10	0.01	0.26	0.03
WC 65JA	1,509	0.18	0.10	0.73	0.38
WC 71D	135	0.22	0.01	0.40	0.02
WD 45A	2,984	1.05	1.10	1.50	1.57
WD 73A	20,159	0.39	2.78	0.61	4.33
WD 89A	5,000	0.10	0.18	0.22	0.39
Total	175,510		22.6		37.6

The previous chapter discussed the impact of outliers and how they might influence overall averages. The approach used in this chapter calculated mass loading separately for each platform. In most instances, the platforms that exhibited outlier concentrations also had relatively low discharge volumes. This means that the calculated mass loadings for those platforms were relatively low and were not counted beyond their reasonable contribution. The effect of this process is to "flow weight" the relative contribution of each discharge. The few platforms that had the highest discharge volumes generally had concentrations that were near or below the mean or median of the data sets. One exception to this trend is the ammonia and TKN results for the high-volume platforms, which were higher than the mean.

Extrapolation of Results to Full Hypoxic Zone

The discharge volumes and loadings in Tables 17-20 represent the contributions of the 50 platforms that were sampled. These are believed to be representative of the full set of hypoxic zone platforms with produced water discharges in terms of the range of concentrations and discharge volumes. In fact, they may err on the side of conservatism for the following reasons:

- Any values reported by the laboratory as "less than X" were counted as being equal to "X," and
- Outlier concentrations for the analyzed parameters were not excluded.

One way of extrapolating the results from Tables 17-20 to estimate produced water discharges and their mass loadings to the full hypoxic zone is to compare the total discharge volume of the 50 sampled platforms with the total discharge volume for the entire hypoxic zone. Unfortunately, the discharge volume for the entire hypoxic zone is not readily available in any of the agency records or databases. It may be available for extraction from hundreds of individual paper files (NPDES Permit Discharge Monitoring Reports submitted by each operator) in the EPA Region 6 offices, but that effort was not practical for this short-timetable project.

An alternative approach is to assume that the volume of produced water generated from the lease blocks located within the hypoxic zone is a reasonable approximation of the volume of produced water actually discharged there. The MMS has records of the produced water generation by lease block (see Appendix E). For 2003, the total water produced from oil zones was 125,122,378 bbl, the total water from gas zones was 60,199,843 bbl, and the total water produced in the hypoxic zone was 185,322,221 bbl. Further assuming that the volume is equally distributed throughout the year, the average daily volume was 507,732 bbl/day for the entire hypoxic zone.

This volume is 2.89 times the volume represented by the 50 sampled platforms (175,510 bbl/day). The loadings from Tables 17-20 can be extrapolated upward by a factor of 2.89 to estimate the total loading for the entire hypoxic zone. Table 21 shows the full loading estimates.

Table 21 – Extrapolation of Loading Estimates to Entire Hypoxic Zone

Parameter	Loading from Sampled Platforms (lb/day)	Estimated Loading for Entire Hypoxic Zone (lb/day)
BOD	36,000	104,100
TOC	14,100	40,700
Nitrate	68.3	197
Nitrite	3.07	9
Ammonia	4,770	13,800
TKN	5,140	14,900
Orthophosphate	22.6	65
Total phosphorus	37.6	109

Perspective on Relative Contributions

The mass loading of oxygen demand and nutrients from produced water discharges to the hypoxic zone is substantial. Although these numbers appear large, they should be considered in the context of the volume of the hypoxic zone, which is estimated as being 17,000 km^2 in area and an average of 17 m deep. This gives a hypoxic zone volume of 289 km^3 (2.9×10^{11} m^3, or 2.9×10^{14} liters). A discharge loading of 104,000 lb of BOD, if assumed to be evenly diluted throughout the entire hypoxic zone, would contribute only 0.17µg/L, or 0.17 ppb, of additional BOD. The weight of all that water is an equally impressive number. Assuming a weight of 2.2 lb/L (this is the weight of fresh water – salt water is slightly heavier), this equals 6.4×10^{14} lb.

Another important feature is the location at which the produced water is discharged. Virtually all offshore platforms discharge to open ocean environments that are subject to wind and wave action. Discharges that are made anywhere near the surface will receive abundant reoxygenation due to the natural processes. The OOC database included data on the produced water discharge locations. Table 22 shows the percentage of platforms at relatively shallow depths – more than half discharge at or above the surface of the ocean. About 93 percent discharge in the top 20 feet of the water column. This should provide effective mitigation for some of the oxygen-demanding pollutants.

Table 22 – Data on Depth of Discharge Locations

Depth (ft) of Discharge Location	No. of Platforms	% of Platforms from OOC Database
0 or above the surface	154	54
<5	204	71
<10	249	87
<20	267	93

Another important point of perspective is a comparison of the produced water discharge mass loadings to the mass loading of key pollutants from the Mississippi and Atchafalaya Rivers. (Table 23). The riverine loadings are estimated from a National Oceanic and Atmospheric Administration report, Goolsby et al. (1999).[2] That report expresses fluxes in metric tons per year.

Table 23 – Comparison of Nutrient Loadings from Produced Water Discharges and Riverine Inputs

Nutrient	Mean Flux (lb/yr) from Mississippi and Atchafalaya Rivers (Goolsby et al. 1999)	Estimated Annual Mass Loading (lb/yr) from Produced Water Discharges to the Hypoxic Zone	Ratio of Produced Water Loading to Riverine Loading
Ammonia	68,355,000	5,030,000	[a]
Organic N	1,278,900,000	389,000 (calculated as TKN – ammonia)	[a]
Nitrate	2,100,000,000	71,900	[a]
Nitrite	0	3,285	[a]
Total N	3,460,000,000	5,500,000	0.00159
Orthophosphate	92,100,000	23,700	[a]
Particulate phosphate	209,000,000	0	[a]
Total P	301,000,000	39,800	0.00013

[a] The key ratios are total nitrogen and total phosphorus. Ratios for the other component comparisons are not shown.

The produced water discharge loadings are several orders of magnitude smaller than those entering the Gulf of Mexico from the rivers. The total nitrogen loading is about 0.16 percent and the total phosphorus loading is about 0.013 percent of the loading coming from the rivers.

[2] Goolsby, Donald A., William A. Battaglin, Gregory B. Lawrence, Richard S. Artz, Brent T. Aulenbach, Richard P. Hooper, Dennis R. Keeney, and Gary J. Stensland. 1999. Flux and Sources of Nutrients in the Mississippi–Atchafalaya River Basin: Topic 3 Report for the Integrated Assessment on Hypoxia in the Gulf of Mexico. NOAA Coastal Ocean Program Decision Analysis Series No. 17. NOAA Coastal Ocean Program, Silver Spring, MD. 130 pp.

Chapter 6 – QA/QC Evaluation of Data

AccuLab produced data in two different formats. First, for each sample, the laboratory produced a "Report of Analysis." These reports included sample identifiers and sample dates, laboratory receipt dates, and analysis dates. The reports also included the method identification as well as results and result units. Other information provided with these reports included the completed chain-of-custody form, the completed sample log sheet, and the laboratory's sample receipt checklist. Comments were also included, as necessary; however, laboratory QC information was not included in these reports. Secondly, the laboratory provided data in electronic format using Microsoft Excel spreadsheets. The spreadsheets included field and laboratory QC results. Raw data were not included in these deliverables.

Data Quality Evaluation

Sampling Precision: Approximately 12 percent of all samples collected for the project were collected in duplicate, meeting the established requirement of a minimum of 10 percent duplicates. With 82 samples, 10 pairs of field duplicates were taken. The target RPD was 25 percent. With the exception of dissolved and suspended BOD and TOC, the duplicates were analyzed for the same parameters as the samples. Field duplicate results for all parameters in 9 of the 10 duplicate pairs produced RPDs ranging from 0 to 24 percent. In one of the duplicate pairs, the RPD for TKN, o-phosphorus, and total phosphorus was 19, 70, and 38 percent, respectively. In addition, in two of the other duplicate pairs, total phosphorus was detected just above the MQL in one of the duplicate pairs, whereas it was undetected above the MQL in the other. With these minor exceptions, sampling precision was acceptable.

Analytical Precision: An MS/MSD pair was analyzed by the laboratory for every sample batch. For BOD measurements, an LCS/LCSD was analyzed. The target RPD was 25 percent. Comparison of MS/MSD and LCS/LCSD results for the parameters revealed RPDs ranging from 0 to 19 percent. Analytical precision for the study was acceptable.

Bias: Approximately 26 percent of all locations sampled were accompanied by field blanks; this met the established requirement of a minimum of 25 percent field blanks. With the exception of BOD and TOC measurements, field blanks were subject to the same analyses as the samples. In only one case was a parameter detected in a blank at a concentration greater than the reported MQL. The parameter in this case, ammonia, was detected at a concentration of 0.014 mg/L, slightly above the MQL (0.01 mg/L). With sample concentrations ranging between 5 mg/L and over 200 mg/L, blank contamination in this one case is inconsequential.

LRBs were analyzed for all parameters. LRBs for BOD were equal to or less than the 0.2 mg/L reporting level. For all other parameters, LRB concentrations were below the MQL. Bias was acceptable for the data set.

Accuracy: MSs (or LCSs for BOD) were used to assess the accuracy of the analytical measurements. An MS (or LCS for BOD) was performed for every batch. In most cases, the samples used were from the produced water study. The target acceptance limits for recovery is 80-120 percent of the spike concentration. With one exception, recoveries for the parameters ranged from 81 to 120 percent. In one case, TKN, percent recovery was slightly above the acceptance limit, at 126 percent. In this case, the LCS was under control. Hence, QC for the data analyzed within the batch associated with the TKN measurements was acceptable. Accuracy for the study as a whole was acceptable.

Representativeness: The initial sample set, taken from 50 platforms, and agreed to by all participants in the project, was determined to adequately represent the population of platforms in the hypoxic zone. These 50 platforms appear to cover approximately 35 percent of the total volume of produced water discharge to the hypoxic zone. Representativeness for the data set was acceptable.

Comparability: Comparability is a qualitative parameter that pertains to the confidence with which one data set can be compared to another and contribute to a common analysis and interpretation. Sample data should be comparable with other measurement data for similar sites under similar conditions. For example, data sets generated during the present study should be comparable to data collected previously. In order to be comparable, data sets must employ the same or similar methods and should be associated with similar levels of quality assurance and control. No prior data sets of sufficient quality were available to assess this parameter.

Completeness: Completeness is a measure of the amount of useable data obtained, expressed as a percentage of the number of useable measurements intended to be obtained (i.e., data that were planned to be collected). The degree to which a lack of completeness affects the outcome of a study is a function of many factors, and the intensity of effect due to incompleteness is best expressed as a qualitative measure. This QC measure is typically used therefore as a screening tool, with a value of 80 percent complete as a general rule of thumb.

The study focused on 50 platforms located within the hypoxic zone. There were cases where samples were initially taken incorrectly (e.g., placed in the incorrect sample bottle), where initial data produced qualitative results (e.g., original samples unexpectedly depleted oxygen in all BOD tests), where some measurements were inadvertently omitted by the laboratory (e.g., dissolved BOD and dissolved organic carbon were not run), or where an additional sample was required because original results showed high variation. In all these cases, replacement or additional samples were successfully collected and analyzed.

There were four cases where the initial sample pH measured by the laboratory was determined to be exceptionally low. The laboratory surmised that sample container caps may have been switched in the field, giving a falsely low pH for the sample. Sampling personnel on the platforms were subsequently advised to take care not to switch the caps. In addition, the pH of the next sample (for a three-sample platform) was compared to the pH of the initial sample. In all cases, the pH of the following samples was within the expected range. The laboratory also indicated in its report that, if the caps were switched, it is not believed that it would have a large effect on the other test results. These data, though so qualified by the laboratory, are usable.

There was one case in which data intended to be collected was not collected. In one instance where 3 samples were to be taken, the first two samples were successfully taken and analyzed, but the platform ceased produced water discharge before the planned third sample could be taken. This was the only instance in which a planned sample was not taken.

In addition to the above, all other samples taken were properly preserved, analyzed within hold time, and analyzed successfully in compliance with established QC criteria. Hence completeness is determined to be very nearly 100 percent.

Specific Issues: All laboratory Reports of Analysis indicated that “sample for pH was past maximum hold time when received at the laboratory.” At the onset of the sampling program, the difficulty of having platform personnel take properly controlled pH measurements at all of the platforms was recognized. As a result, a decision was made to take this measurement at the laboratory, recognizing the holding time requirement could not be satisfied. As pH was not a key measurement for this study, the lab pH measurement was used, even if it was taken at a time later than desired. The impact on data quality is negligible.

Sample temperature was taken and recorded at the same time as pH, sometime after samples had been removed from the cooler. The laboratory did not also record sample temperature on receipt (i.e., in the sample coolers) as required in AccuLab’s Laboratory Quality Control Measures. However, the AccuLab Sample Receipt Checklist indicates whether the coolers were received with ice present. There was one case in which the coolers were received without ice, and this platform was resampled. All other coolers were received with ice present. Since ice was present in the coolers on receipt, sample temperatures are assumed to meet method requirements (<4°C).

Logically, TKN measurements should produce results that are greater than or equal to ammonia concentrations in every case. However, in three instances, data were produced for which TKN concentrations were less than those of ammonia. In these cases, the laboratory reran the TKN analyses and generated TKN results that were greater than ammonia concentrations. These rerun TKN analyses were, however, run after the maximum sample holding times. The laboratory noted this information in the spreadsheets provided. The original data for these measurements were retained in the project database as flagged data.

<u>Conclusions of Data Evaluation</u>

With the minor exceptions noted above, the overall quality of the data collection activity was acceptable.

Chapter 7 – Findings and Conclusions

The report describes and presents the results of a program to sample 50 offshore oil and gas platforms located within the Gulf of Mexico hypoxic zone. The program was conducted in response to a requirement in the EPA general NPDES permit for offshore oil and gas discharges (GMG290000). EPA desired information on the amount of oxygen-demanding substances contained in the produced water discharges. This information was needed as inputs to several water quality models that EPA intends to run to estimate the impact of the produced water discharges on the hypoxic zone.

The sampling program was completed successfully on a very short timetable. The logistics were complicated by:

- Working with 50 different facilities operated by more than 20 oil and gas companies,
- Dealing with offshore conditions and transportation issues, and
- Arranging timely transfer of collected samples from platforms to shore bases to couriers to the testing laboratory within a 48-hour period.

This involved frequent and extensive coordination among several agencies, the industry, two analytical laboratories, and Argonne National Laboratory.

The results show that there is variability over time at any given platform, but that the variability is not excessive. The study evaluated variability of BOD for 16 platforms that were tested more than once. All but one of these platforms (about 94 percent) passed the variability criterion established for the study. The one platform exhibiting excessive variability was sampled six times and was unable to show consistent results. The concentrations of BOD and the other oxygen-demanding materials vary from platform to platform, too. Most of the sample results fell within a fairly restricted range of values, but for each parameter, there were several outlier samples that had values much higher than the range for the rest of the samples.

The sampling provided average platform concentrations for each parameter. These were converted to mass loadings by multiplying by the discharge volume and a conversion factor. The mass loadings represent estimates of the lb/day of each parameter that are discharged from the 50 platforms. The total produced water discharge volume from the 50 platforms was 175,510 bbl/day. The total amount of produced water generated in the hypoxic zone was estimated as 507,732 bbl/day. Finally, the mass loadings from produced water discharges to the entire hypoxic zone were estimated by multiplying the 50-platform loadings by the ratio of total water generated to 50-platform discharge volume.

The produced water discharge loadings estimated for the entire hypoxic zone are several orders of magnitude smaller than those entering the Gulf of Mexico from the Mississippi and Atchafalaya Rivers. The total nitrogen loading is about 0.16 percent and the total phosphorus loading is about 0.013 percent of the nutrient loading coming from the rivers.

These estimates and the sampling data from 50 platforms represent the most complete and comprehensive effort ever undertaken to evaluate the oxygen-demanding parameters contained in produced water discharges.

Acknowledgments

Argonne's work was sponsored by DOE's National Energy Technology Laboratory (NETL). Nancy Comstock is the NETL project officer. She and Nancy Johnson of DOE's Office of Fossil Energy participated in the planning meetings leading up to the sampling program and reviewed information throughout the study. We acknowledge the support and assistance of Margaret Metcalf from the MMS, who provided extensive data sets and maps that were used in selecting platforms.

This work was closely coordinated with API, the OOC, and more than 20 oil and gas companies and their support contractors. The companies that had their platforms sampled include: Apache, ATP, Bois D'Arc, BP, ChevronTexaco, Dominion, El Paso, Energy Resource Technology, ENI, ExxonMobil, Houston Exploration, Hunt Petroleum, Linder, Mariner, Newfield, Nexen, Northstar, Seneca, Stone, and W&T Offshore. We thank the environmental coordinators, platform personnel, helicopter pilots, and shore base managers who contributed their time to make sure we got representative samples on schedule. In particular, we acknowledge the frequent guidance and assistance of Shell's Kent Satterlee, who is the chairman of the OOC Environmental Subcommittee, and ExxonMobil's Michael Parker, who served as liaison to API.

Finally, we acknowledge the contributions of Tony Albert of AccuLab and Richard Ricau and David Daniel of EEUSA. Without their hard work and extra effort, we would not have been able to accomplish all of the sampling included in this program in such a short amount of time.

Appendix A – Sampling Instructions for Produced Water Study

General Instructions

1. Environmental Enterprises will prepare and send sampling kits for this study prior to the start date. There will be three different kits used for this sampling project. All sampled sites will use the same basic kit. Ten percent of the sampled sites will include a field duplicate sample, and twenty-five percent of the sampled sites will include a field blank sample. When the kit or kits arrive, check the contents. Wear a pair of CLEAN gloves when handling any of the items in the kit.

   1.1. All kits will have:

- 1 bottle marked BOD, Nitrate, Nitrite, ortho-Phosphate, Conductivity, Salinity, pH.
- 1 bottle marked TOC, TKN, Ammonia, Total Phosphorus. This bottle will contain a small amount of dilute sulfuric acid. Check to make sure the acid is present by holding the bottle to the light. Do not remove cap to look inside. The acid should be visible at the bottom of the bottle.
- 1 MSDS for sulfuric acid.
- 1 thermometer.
- 2 plastic bags.
- 2 Chain of Custody forms with instructions for completion on the back. One of the Chain of Custody forms will be an extra in case the first becomes unusable.
- 2 Sampling Log sheets with instructions for completion on the back. One of the Sampling Log sheets will be an extra in case the first becomes unusable.

   1.2. If the kit includes collection of Field Duplicate samples, it will also have:

- 1 bottle marked FIELD DUPLICATE BOD, Nitrate, Nitrite, ortho-Phosphate, Conductivity, Salinity, pH.
- 1 bottle marked FIELD DUPLICATE TOC, TKN, Ammonia, Total Phosphorus. This bottle will contain a small amount of dilute sulfuric acid. Check to make sure the acid is present by holding the bottle to the light. Do not remove cap to look inside. The acid should be visible at the bottom of the bottle.

   1.3. If the kit includes collection of Field Blank samples, it will also have:

- 1 bottle marked FIELD BLANK BOD, Nitrate, Nitrite, Orthophosphate, Conductivity, Salinity, pH.
- 1 bottle marked FIELD BLANK TOC, TKN, Ammonia, Total Phosphorus. This bottle will contain a small amount of dilute sulfuric acid. Check to make sure the acid is present by holding the bottle to the light. Do not remove cap to look inside. The acid should be visible at the bottom of the bottle.
- 2 bottles marked Deionized Water Lot Number *mmddyyyy*, which indicates the date that the deionized water was drawn.

2. If any of the items listed above are missing, call Richard Ricau or other Sample Department personnel (Environmental Enterprises) at (800) 966-2788 or (985) 646-2787 to get instructions as to how to proceed.

Sampling Instructions (For actual samples, field duplicates, and field blanks, make sure you follow your company and facility health and safety plan.)

3. Please call Richard Ricau or other Sample Department personnel (Environmental Enterprises) at (800) 966-2788 or (985) 646-2787 to confirm scheduled pick up and coordinate delivery to AccuLab via Environmental Enterprises USA (EEUSA) pick up service, Federal Express, or Hot-Shot. If you have any questions about sample pick up, call Richard Ricau or other Sample Department personnel at (800) 966-2788 or (985) 646-2787.

4. If you have any questions about these instructions or if samples cannot be delivered to AccuLab within 36 hours of collection, please call Charmiane Albert or Erica Dragon (AccuLab) at (504) 371-8557.

5. Enter the requested general information on the Chain of Custody form if it has not already been entered. Refer to the instructions on the back of the Chain of Custody form.

6. Take the kit to the sample location where monthly produced water compliance samples are taken (overboard water discharge). If you are not already wearing gloves, put them on now.

7. Take the two sample bottles out of the kit and mark the sample location (area, block, platform) on each label in INDELIBLE ink (Sharpie or other similar pen).

   7.1. If the kit includes collection of Field Duplicate samples, also take the two sample bottles marked FIELD DUPLICATE out of the kit and mark the sample location on each label in INDELIBLE ink (Sharpie or other similar pen).

   7.2. If the kit includes collection of Field Blank samples, also take the two sample bottles marked FIELD BLANK out of the kit and mark the sample location on each label in INDELIBLE ink (Sharpie or other similar pen).

8. Open the sample spigot or needle valve and let the water run for at least 2 minutes to be sure that any stagnant water standing in the pipe or spigot is flushed.

9. Do not rinse any of the sample bottles. Collect a sample in the bottle marked TOC, TKN, Ammonia, Total Phosphorus. Fill the bottle to the bottom of the neck. TAKE SPECIAL CARE NOT TO OVERFLOW THE BOTTLE, AS IT CONTAINS ACID. Cap it tightly. Immediately after this, collect a sample in the bottle marked BOD, Nitrate, Nitrite, ortho-Phosphate, Conductivity, Salinity, pH. Fill it to the bottom of the neck and cap it tightly.

   9.1. If the kit includes collection of Field Duplicate samples, also collect samples in the two sample bottles marked FIELD DUPLICATE in the same way.

9.2. If the kit includes collection of Field Blank samples, carefully pour the deionized water from one of the deionized water bottles into one of the bottles marked FIELD BLANK and the deionized water from the other bottle into the other bottle marked FIELD BLANK. This procedure provides a check on external contamination. <u>DO NOT ADD ANY PRODUCED WATER TO THESE BOTTLES</u>! REMEMBER TO TAKE CARE WHEN POURING THE DEIONIZED WATER INTO THE BOTTLE THAT CONTAINS ACID.

10. Dry off the outside of all filled sample bottles with a paper towel and cover the label with clear plastic tape.

11. Check the boxes on the Chain of Custody form under Testing Required & Preservative. Circle YES or NO to indicate whether the sample kit included bottles for FIELD BLANK or FIELD DUPLICATE and whether you collected the required samples.

12. Within 15 minutes of when you collected the samples, and using the supplied thermometer, measure the temperature of the sample(s) marked BOD, Nitrate, Nitrite, ortho-Phosphate, Conductivity, Salinity, pH. If possible, collect a portion of sample in a separate clean container, and analyze it rather than the sample itself. Record the results along with the date and time measured and your initials.

13. Enter the date and time the samples were collected and print and sign your name in the appropriate space on the Chain of Custody form. Complete the Sampling Log sheet, including date, time, and signature. An example of a completed sheet is shown on the back.

14. Chill the sample(s) in a refrigerator or an ice bath before packaging for transport.

14.1. In order to prevent water leakage, open plastic bags provided. Place newspapers or other absorbent material on the bottom of the ice chest. **PLACE ONE WATERPROOF BAG** in the ice chest. Put the tightly capped sample containers in the second plastic bag and tie it off securely. Place the bag with the samples inside the other bag and **<u>fill the outside bag with ice.</u> Close the outside plastic bag and TIE IT OFF SECURELY.** Place newspapers or other absorbent material on top of the bags to absorb any condensation from inside the cooler.

14.2. Tape the ice chest closed but allow access to the chest for ice to be replenished at each transfer, if necessary.

14.3. Place the Chain of Custody and Sampling Log sheet in its Ziploc bag along with these instructions and tape the Ziploc bag to the outside of the ice chest. Make sure that the documents can be easily removed and replaced.

15. When you give the kit to someone (helicopter pilot, crew boat captain, shore base personnel), sign the Chain of Custody form and enter the date and time in the appropriate spaces. Refer to the instructions on the back of the Chain of Custody form, Steps 19 and 20.

16. Explain to the person receiving the ice chest that he must sign the Chain of Custody form to receive the samples and that he must relinquish the ice chest for the next person, as you did.

17. **Each person that takes custody of the sample(s) must complete his part of the COC (collected by & relinquished by or received by & relinquished by)**.

    17.1. Shore base personnel should open the cooler upon receipt to replenish the ice in the cooler for the transport of the samples to the laboratory.

18. **Remember that the samples MUST arrive at AccuLab within 36 hours of when they were collected**. **They should arrive within 24 hours, if possible.**

Appendix B – Sampling Log Sheet

THE PERSON COLLECTING THE SAMPLES SHOULD COMPLETE THIS FORM DURING THE SAMPLING ACTIVITY, MAKE A COPY FOR HIS/HER RECORDS, AND PLACE THE ORIGINAL IN THE ZIP LOCK BAG ALONG WITH THE CHAIN OF CUSTODY FORM. PLEASE PRINT NEATLY!

PRODUCED WATER STUDY – SAMPLING LOG ENTRY FORM

ITEM	LOG ENTRY
PLATFORM NAME/NUMBER	
DATE/TIME SAMPLING BEGAN	
NAME OF LEAD SAMPLER	
NAME OF SUPPORT SAMPLERS (IF ANY)	
WAS SAMPLING LOCATION INDOORS OR OUTDOORS?	
IF OUTDOORS, INDICATE WEATHER CONDITIONS?	
SAMPLE ID - SAMPLE A	
SAMPLE A TEMPERATURE	
OBSERVATIONS, SAMPLE A (CLARITY, COLOR, ODOR, ETC.)	
SAMPLE ID - SAMPLE B	
OBSERVATIONS, SAMPLE (CLARITY, COLOR, ODOR, ETC.)	
IF FIELD DUPLICATE SAMPLES ARE MADE, PROVIDE SAMPLE IDS.	
IF FIELD BLANK SAMPLES ARE MADE, PROVIDE SAMPLE IDS.	
DESCRIBE GENERAL SAMPLING PROCEDURE.	
COMMENTS (NA IF NONE)	
DATE/TIME SAMPLING ENDED	
SIGNATURE OF LEAD SAMPLER	

Appendix C – Chain-of-Custody Form

Chain of Custody Record

AccuLab Inc.
5041 Taravella Road
Marrero, LA 70072
Phone (504) 371-8557
Fax (504) 371-8560
acculab@acculabnola.com

Client	1
Contact	2
Address	3
City, State, Zip	4
Phone Number	5
Fax Number	6
Kit #	7

Discharge Area, Block, and Platform	Sampler's Name (print and sign)	Due Date
8	9	ROUTINE

Testing Required & Preservative

Matrix: P = Potable Water W = Water/Wastewater S = Soil Sl = Sludge O = Oil G = Glycol PC = Paint Chips Ot = Other (describe in remarks)
Preservatives: A = Cool, 4°C B = Cool, 4°C, Sulfuric Acid to pH <2 C = Cool, 4°C, Nitric Acid to pH <2 D = Other (describe in remarks) E = Cool, 4°C, Sodium Thiosulfate F = Cool, 4°C, HCl to pH <2

AccuLab #	Date	Time	Grab	Sample Location	Matrix	# of Containers	BOD, Nitrate, Nitrite, ortho-Phosphate, Conductivity, Salinity, pH A	TOC, TKN, Ammonia, Total Phosphorus B	
	10	11	XX	12	W		13	14	

Does this kit include bottles for a field blank? YES NO If yes, were the samples taken? YES NO
Does this kit include bottles for a field duplicate? YES NO If yes, were the samples taken? YES NO

Remarks: Temp = 15

Temp Date Analyzed: 16 Time Analyzed: 17 Analyzed by: 18

Lot Number of Containers used (entered by lab):

Lot Number of Sulfuric Acid used (entered by lab):

			Did you replenish the ice? Yes	No
Relinquished by (Signature) 19	Date/Time 20	Received By (Signature) 21	22	23
Relinquished by (Signature) 24	Date/Time 25	Received By (Signature) 26	27	28
Relinquished by (Signature)	Date/Time	Received By (Signature)		
Relinquished by (Signature)	Date/Time	Received By (Signature)		
Relinquished by (Signature)	Date/Time	Received for Lab By (Signature)		
	Samples on ice when received at lab? YES NO			
Relinquished by (Signature)	Date/Time	Received By (Signature)		

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Appendix D – Sample Results

Due to the large number of parameters, the results are split into two long tables. The first table (D-1) provides the details on platform location, operator, sampling date, BOD, and TOC. The second table (D-2) provides the results for all other parameters. Rather than repeat the full platform location data and sampling date, the second table uses only the platform ID as the identifier.

Table D-1 – Sample Results for BOD and TOC

Block & Platform	Operator	Lease	Sample Date	BOD, mg/L	Dissolved BOD, mg/L	Suspended BOD, mg/L	TOC, mg/L	Dissolved TOC, mg/L	Suspended TOC, mg/L
EC 46B	Stone Energy	3288	6/1/2005	732	NA	NA	412	NA	NA
EC 47JP	Newfield	00768-47,48a	2/23/2005	1335	NA	NA	765	NA	NA
EC 47JP	Newfield	00768 47, 48a	3/16/2005	787	NA	NA	480	NA	NA
EC 47JP	Newfield	00768 47, 48a	4/13/2005	740	NA	NA	450	NA	NA
EC 49B	Newfield	01364	5/18/2005	1200	1128	72	630	620	10
EI 107A	Apache	G15241	2/25/2005	330	NA	NA	97.0	NA	NA
EI 107A	Apache	G15241	3/16/2005	200	NA	NA	440	NA	NA
EI 107A	Apache	G15241	4/21/2005	213	NA	NA	43.0	NA	NA
EI 128A-JC	Energy Res. Tech	OCS 0442	4/26/2005	415	NA	NA	86	NA	NA
EI 172A	Newfield	5494	5/18/2005	1821	NA	NA	720	NA	NA
EI 175B	Apache	G00438	5/26/2005	392	NA	NA	172	NA	NA
EI 184A	Newfield	5498	5/18/2005	628	NA	NA	178	NA	NA
EI 50-1	Hunt Petroleum	G17960	4/20/2005	147	NA	NA	4880	NA	NA
EI 57A	Northstar Gulfsand	2601	5/12/2005	503	NA	NA	325	NA	NA
EI 74A	Chevron Texaco	G02099	5/18/2005	442	NA	NA	174	NA	NA
EI 95F	W&T Offshore	0046	2/25/2005	150	NA	NA	50.0	NA	NA
EI 95F	W&T Offshore	0046	3/24/2005	214	NA	NA	122	NA	NA
EI 95F	W&T Offshore	0046	4/21/2005	79	NA	NA	<50	NA	NA
GI 19# 3	ExxonMobil	00033	2/21/2005	488	NA	NA	122	NA	NA
GI 19#3	ExxonMobil	00033	3/15/2005	482	NA	NA	152	NA	NA
GI 19#3	ExxonMobil	00033	4/19/2005	592	535	57	179	169	10
HI 37A	Seneca	G15769	5/31/2005	5378	NA	NA	2440	NA	NA
HI 39A	Houston Expl	04078	5/25/2005	1224	NA	NA	755	NA	NA
HI 46A	Mariner	G24404	5/24/2005	11108	NA	NA	4700	NA	NA
SM 238-190	El Paso Prod	00310	5/23/2005	940	NA	NA	545	NA	NA
SM 268A	Apache	G02310	2/24/2005	626	NA	NA	224	NA	NA
SM 268A	Apache	G02310	4/13/2005	578	432	146	248	121	127
SM 40JA	Hunt Petroleum	G13607	4/21/2005	582	NA	NA	2290	NA	NA
SMI 23G	Devon Energy	G00778	5/11/2005	876	NA	NA	374	NA	NA

Table D-1 – Sample Results for BOD and TOC

Block & Platform	Operator	Lease	Sample Date	BOD, mg/L	Dissolved BOD, mg/L	Suspended BOD, mg/L	TOC, mg/L	Dissolved TOC, mg/L	Suspended TOC, mg/L
SMI 268A	Apache	G02310	3/16/2005	504	NA	NA	236	NA	NA
SMI 33D	Apache	G00780	5/5/2005	289	233	56	162	156	6
SS 108D	ChevronTexaco	00814	3/29/2005	1392	NA	NA	730	NA	NA
SS 108D	ChevronTexaco	00814	4/19/2005	1155	NA	NA	590	NA	NA
SS 157A	Newfield	8709	5/23/2005	1108	NA	NA	625	NA	NA
SS 169C	ChevronTexaco	00820	3/24/2005	561	NA	NA	186	NA	NA
SS 169C	ChevronTexaco	00820	4/19/2005	656	NA	NA	254	NA	NA
SS 182C	ChevronTexaco	00821	3/24/2005	331	NA	NA	116	NA	NA
SS 182C	ChevronTexaco	00821	4/19/2005	432	NA	NA	119	NA	NA
SS 182E	Chevron Texaco	G01019	5/17/2005	344	328	16	111	NA	NA
SS 189A	Apache	G04232	5/17/2005	711	NA	NA	286	NA	NA
SS 191B	Hunt Pet.	G22713	4/28/2005	974	NA	NA	448	NA	NA
SS 58A	Newfield	G07746	2/23/2005	636	NA	NA	87.5	NA	NA
SS 58A	Newfield	G07746	3/16/2005	350	NA	NA	74	NA	NA
SS 58A	Newfield	G07746	4/13/2005	512	NA	NA	286	NA	NA
SS108D	ChevronTexaco	00814	2/23/2005	1010	NA	NA	140	NA	NA
SS169C	ChevronTexaco	00820	2/23/2005	678	555	123	157	107	50
SS182C	ChevronTexaco	00821	2/23/2005	366	NA	NA	62.0	NA	NA
ST 148E	Newfield	G01898	2/23/2005	1134	NA	NA	140	NA	NA
ST 148E	Newfield	G01898	3/16/2005	942	NA	NA	665	NA	NA
ST 161A	Apache	G01248	5/12/2005	543	NA	NA	240	NA	NA
ST 164C	Stone Energy	1250	5/10/2005	372	NA	NA	168	NA	NA
ST 34A	Bois d'Arc	4842	5/3/2005	103	NA	NA	49.5	NA	NA
VR 119G	W&T Offshore	00487	3/4/2005	1725	NA	NA	880	NA	NA
VR 119G	W&T Offshore	00487	3/24/2005	1173	NA	NA	805	NA	NA
VR 119G	W&T Offshore	00487	4/21/2005	1446	NA	NA	810	NA	NA
VR 164A	ExxonMobil	G06668	2/23/2005	41	NA	NA	66.0	NA	NA
VR 164A	ExxonMobil	G06668	3/24/2005	704	NA	NA	280	NA	NA
VR 164A	ExxonMobil	G06668	4/12/2005	748	NA	NA	280	NA	NA
VR 164A	ExxonMobil	G06668	5/26/2005	108	NA	NA	44.5	NA	NA
VR 164A	ExxonMobil	G06668	6/23/2005	1713	NA	NA	935	NA	NA
VR 164A	ExxonMobil	G06668	6/29/2005	186	NA	NA	92.0	NA	NA
VR 22B	Energy Res. Tech.	2865	5/24/2005	879	NA	NA	374	NA	NA
WC 102G	BP	00247	3/2/2005	529	400	129	166	137	29

Table D-1 – Sample Results for BOD and TOC									
Block & Platform	Operator	Lease	Sample Date	BOD, mg/L	Dissolved BOD, mg/L	Suspended BOD, mg/L	TOC, mg/L	Dissolved TOC, mg/L	Suspended TOC, mg/L
WC 102G	BP	00247	3/23/2005	328	NA	NA	218	NA	NA
WC 102G	BP	00247	4/20/2005	579	NA	NA	288	NA	NA
WC 110A	BP	00081	3/2/2005	584	NA	NA	280	NA	NA
WC 110A	BP	00081	3/23/2005	614	NA	NA	374	NA	NA
WC 110A	BP	00081	4/20/2005	792	738	54	370	354	16
WC 130A	Dominion E&P	12761	5/4/2005	804	NA	NA	324	NA	NA
WC 168A	Linder Oil	5238	5/4/2005	80	NA	NA	25.6	NA	NA
WC 170A	Nexen Pet.	OCS-G 4085	4/27/2005	198	NA	NA	88.5	NA	NA
WC 173K	Houston Expl	00759	5/18/2005	736	NA	NA	320	NA	NA
WC 215A	Energy Res. Tech	OCS-G-4087	5/2/2005	826	NA	NA	356	NA	NA
WC 237A	ATP Oil & Gas	02833	5/4/2005	1632	NA	NA	990	NA	NA
WC 53A	El Paso Prod.	G04379	5/11/2005	167	132	35	71.5	66.5	5.0
WC 65JA	BP	G02825	3/2/2005	464	NA	NA	31.6	NA	NA
WC 65JA	BP	G02825	3/23/2005	299	NA	NA	29.8	NA	NA
WC 65JA	BP	G02825	4/20/2005	405	NA	NA	124	NA	NA
WC 71D	BP	00244	4/20/2005	494	NA	NA	206	NA	NA
WD 45A	Nexen Pet.	OCS-G 0138	4/28/2005	477	NA	NA	176	NA	NA
WD 73A	ExxonMobil	G01083	2/23/2005	414	NA	NA	61.0	NA	NA
WD 73A	ExxonMobil	G01083	3/16/2005	272	NA	NA	188	NA	NA
WD 73A	ExxonMobil	G0183	4/27/2005	408	NA	NA	154	NA	NA
WD 89A	ENI Petro.	OCS-G 1088	5/4/2005	654	NA	NA	110	NA	NA

Table D-2 – Sample Results for Parameters Other Than BOD and TOC										
Block & Platform	Nitrate, mg/L	Nitrite, mg/L	Ammonia, mg/L	TKN, mg/L	o-Phosphate, mg/L	Total Phosphorus, mg/L	Temperature, ^{o}C [a]	pH, SU	Conductivity, μmhos/cm	Salinity, ppt
EC 46B	2.0	<0.05	30	36.6	0.50	0.62	58	7.25	55000	48.8
EC 47JP	<0.6	<0.05	74.2	76.2	8.10	10.6	25	5.24[b]	67280	58.7
EC 47JP	<0.6	<0.05	54.2	73.6	0.16	2.50	19	6.86	67800	59
EC 47JP	2.0	<0.05	132	140	0.35	2.80	27	6.68	64400	57.8
EC 49B	1.8	<0.05	20.2	32.0	0.27	0.50	32	6.74	50600	37.0
EI 107A	<0.6	<0.05	115	122	<0.10	<0.20	26	5.56	168200	245.4
EI 107A	<0.6	<0.05	99.0	116	<0.10	<0.20	27	5.79	152500	244
EI 107A	<0.6	<0.05	209	216	0.28	0.50	32	5.50	134400	242.7
EI 128A-JC	1.7	<0.05	183	192	<0.10	<0.20	45	6.49	153400	190.4
EI 172A	4.0	<0.05	36.4	42.0	<0.10	<0.20	25	5.14	60500	48.8
EI 175B	2.8	<0.05	85.8	106	0.13	0.28	40	6.74	129250	165.1
EI 184A	<0.6	<0.05	109	113	0.27	0.40	60	6.25	165000	217.5
EI 50-1	<0.6	<0.05	79.2	79.0	0.51	0.64	23	4.12 [b]	15120	10.8
EI 57A	<0.6	<0.05	140	154	<0.10	<0.20	32	6.16	144000	180.5
EI 74A	0.9	<0.05	102	111	0.12	0.38	30	6.48	121000	140.8
EI 95F	1.5	<0.05	77.8	92.0	0.20	0.31	32	6.55	156600	241.8
EI 95F	0.7	<0.05	54.2	57.6	0.17	<0.20	33	6.68	159600	248
EI 95F	1.6	<0.05	132	136	0.17	0.42	33	6.43	156800	261.7
GI 19 #3	<0.6	<0.05	103	111	0.44	0.56	28	6.66	123900	136.3
GI 19#3	1.3	<0.05	99.4	103	<0.10	0.60	28	6.63	124300	141
GI 19#3	<0.6	<0.05	135	142	0.45	0.58	32	6.72	123200	142.6
HI 37A	12.5	<0.05	14.8	20.2	0.12	<0.20	29	6.32	9900	6.5
HI 39A	15.8	<0.05	27.2	37.2	<0.10	0.36	28	6.42	57200	46.0
HI 46A	<0.6	<0.05	22.4	30.6	<0.10	<0.20	30	6.92	48400	39.7
SM 238-190	1.4	<0.05	69.0	80.0	<0.10	0.22	25	6.91	88000	83.9
SM 268A	1.7	<0.05	64.4	74.0	0.23	0.28	48	6.66	133400	160.6
SM 268A	<0.6	<0.05	106	118	0.18	0.36	45	6.48	123200	166.9
SM 40JA	0.8	<0.05	97.8	120	0.11	0.30	40	4.74	120400	132.6
SMI 23G	1.2	<0.05	104	109	<0.10	0.22	31	6.29	120000	136.3
SMI 268A	2.1	<0.05	63.0	66.0	0.16	0.42	43	6.86	129950	177
SMI 33D	<0.6	<0.05	51.4	46.0 [c]	0.26	0.30	29	6.99	65540	54.2
SS 108D	0.6	<0.05	40.0	67.4	0.10	<0.20	29	6.56	108300	117
SS 108D	<0.6	<0.05	107	122	0.16	0.28	42	6.74	100800	119.1
SS 157A	1.9	<0.05	63.4	73.0	0.12	0.26	40	6.73	88000	86.6

Table D-2 – Sample Results for Parameters Other Than BOD and TOC

Block & Platform	Nitrate, mg/L	Nitrite, mg/L	Ammonia, mg/L	TKN, mg/L	o-Phosphate, mg/L	Total Phosphorus, mg/L	Temperature, °C [a]	pH, SU	Conductivity, µmhos/cm	Salinity, ppt
SS 169C	0.7	<0.05	50.2	59.4	0.12	<0.20	41	6.80	114000	144
SS 169C	<0.6	<0.05	110	131	0.43	0.54	47	6.43	117600	148.9
SS 182C	0.8	<0.05	54.2	88.6	0.24 [d]	<0.20 [d]	42	6.77	119700	144
SS 182C	<0.6	<0.05	119	147	0.11	0.32	42	6.68	123200	135.4
SS 182E	<0.6	<0.05	100	110	<0.10	<0.20	44	6.72	115500	127.2
SS 189A	0.7	<0.05	121	128	0.15	0.32	80	6.53	136800	176.9
SS 191B	1.0	<0.05	101	178	<0.10	0.20	65	6.19	135700	217.5
SS 58A	<0.6	<0.05	75.4	82.0	0.31	6.80	40	6.24	98600	106.5
SS 58A	0.9	<0.05	47.4	51.2	<0.10	<0.20	38	3.69 [b]	73450	185
SS 58A	<0.6	<0.05	95	110	<0.10	0.26	40	6.56	100800	108.3
SS108D	3.8	<0.05	76.4	87.0	0.65	0.76	42	6.85	115050	119.1
SS169C	2.8	<0.05	102	107	0.30	0.46	42	6.65	129800	143.5
SS182C	1.6	<0.05	98.8	102	0.11	0.32	40	6.89	118000	132.7
ST 148E	3.5	<0.05	129	134	0.13	0.22	40	6.08	156750	203.9
ST 148E	2.6	<0.05	123	144	0.10	0.30	40	6.34	146900	211
ST 161A	1.1	<0.05	160	168	<0.10	0.20	70	5.89	141000	167.8
ST 164C	0.7	<0.05	80.8	84.2	2.80	3.0	37	6.67	70800	70.4
ST 34A	<0.6	<0.05	37.8	36.2 [e]	0.16	0.28	37	5.88	39440	31.6
VR 119G	0.6	<0.05	33.4	39.8	0.38	0.76	20	7.28	79800	65.0
VR 119G	1.1	<0.05	16.3	28.0	0.25	0.40	35	7.06	79800	73
VR 119G	0.7	<0.05	36.2	43.0	0.61	0.82	35	7.42	78400	70.4
VR 164A	<0.6	0.08	4.58	5.80	0.31	0.40	31.6	6.94	11210	7.2
VR 164A	0.9	<0.05	47.0	51.2	<0.10	<0.20	36	6.45	134400	165
VR 164A	<0.6	<0.05	101	118	<0.10	<0.20	35	6.27	128800	163.3
VR 164A	0.7	<0.05	7.9	11.7	0.12	0.22	26	6.72	22550	17.2
VR 164A	57.5	<0.05	58.0	62.8	<0.10	<0.20	28	5.51	99000	107
VR 164A	7.0	<0.05	4.81	5.46	<0.10	<0.20	30	6.49	51700	42.4
VR 22B	2.4	<0.05	27.2	35.8	<0.10	<0.20	24	6.63	29425	19.9
WC 102G	2.2	<0.05	21.0	24.2	0.11	0.38	16	6.06	34200	27.1
WC 102G	0.8	<0.05	6.75	9.62	<0.10	3.40	30	6.15	912	0.5
WC 102G	1.6	<0.05	14.2	18.7	<0.10	<0.20	22	5.58	560	0.3
WC 110A	0.9	<0.05	34.2	38.8	<0.10	<0.20	16	6.48	51300	45.1
WC 110A	2.2	<0.05	22.5	24.4	<0.10	<0.20	20	6.61	54150	44
WC 110A	1.7	<0.05	51.0	51.0	0.21	0.36	25	6.16	53200	45.1
WC 130A	1.4	<0.05	16.0	16.9	<0.10	<0.10	25	5.83	11190	7.1

Table D-2 – Sample Results for Parameters Other Than BOD and TOC										
Block & Platform	Nitrate, mg/L	Nitrite, mg/L	Ammonia, mg/L	TKN, mg/L	o-Phosphate, mg/L	Total Phosphorus, mg/L	Temperature, ^{o}C [a]	pH, SU	Conductivity, μmhos/cm	Salinity, ppt
WC 168A	4.4	<0.05	15.7	16.8	0.20	0.27	22	6.98	41810	28.9
WC 170A	<0.6	<0.05	43.0	56.0	<0.10	<0.20	45	6.91	69620	55.1
WC 173K	4.2	<0.05	31.8	42.2	<0.10	<0.20	29	6.52	51700	39.7
WC 215A	<0.6	<0.05	51.0	60.0	6.60	7.90	62	6.94	60180	46.9
WC 237A	4.3	<0.05	48.0	49.6	0.11	0.12	23	6.45	48590	36.1
WC 53A	0.8	<0.05	20.2	40.2	<0.10	0.26	32	5.72	360	0.1
WC 65JA	<0.6	<0.05	35.2	37.2	0.15	1.44	60	6.15	85500	85.7
WC 65JA	0.9	<0.05	21.8	26.2	0.20	0.36	58	6.73	79800	84
WC 65JA	<0.6	<0.05	42.6	48.0	0.20	0.38	58	6.50	81200	81.2
WC 71D	<0.6	<0.05	58.8	63.5	0.22	0.40	28	6.56	95200	104.7
WD 45A	2.9	<0.05	96.4	101	1.05	1.50	52	1.77 [b]	84960	79.4
WD 73A	<0.6	<0.05	93.4	97.6	0.34	0.40	42	6.75	104400	99.3
WD 73A	2.6	<0.05	82.0	91.0	0.41	0.94	37	7.10	96050	105
WD 73A	1.0	<0.05	191	198	0.43	0.50	41.5	7.32	99120	105.6
WD 89A	<0.6	<0.05	246	216 [f]	0.10	0.22	46	6.50	127600	148.9

[a] The temperatures were measured in the field by personnel on the platforms. Although temperature should have been reported as ^{o}C, it is likely that some of the values were actually ^{o}F.
[b] Sample container caps may have been switched in the field, giving a falsely low pH for the sample.
[c] Apparent logical inconsistency. TKN > ammonia. Samples reanalyzed on 6/6/05 after hold time was exceeded; the result was 55.0 mg/L.
[d] Apparent logical inconsistency. Total phosphorus sample rerun with the same result. Orthophosphate sample past holding time, so sample was not rerun.
[e] Apparent logical inconsistency. TKN > ammonia. Samples reanalyzed on 6/6/05 after hold time was exceeded; the result was 42.6 mg/L.
[f] Apparent logical inconsistency. TKN > ammonia. Samples reanalyzed on 6/6/05 after hold time was exceeded; the result was 250 mg/L.

Appendix E – MMS Data on Produced Water Production by Lease during 2003

Lease Block	Water from Oil Zones (bbl)	Water from Gas Zones (bbl)	Total Water (bbl)	Lease Block	Water from Oil Zones (bbl)	Water from Gas Zones (bbl)	Total Water (bbl)	Lease Block	Water from Oil Zones (bbl)	Water from Gas Zones (bbl)	Total Water (bbl)
BM 2	294,570	78	294,648	PL 1	150,971	16,845	167,816	ST 162	0	828	828
EC 9, 14	43,980	202,187	246,167	PL 2	0	142,314	142,314	ST 163	0	2,042	2,042
EC 14	0	98,346	98,346	PL 5	0	33,539	33,539	ST 164	30,017	978,966	1,008,983
EC 23	0	65,622	65,622	PL 6	0	1,790	1,790	ST 165	0	41,965	41,965
EC 24	0	2,806	2,806	PL 8	366,801	4,155	370,956	ST 169	679,296	1,749	681,045
EC 32	0	14,922	14,922	PL 9	22,776	57,861	80,637	ST 170	0	7,451	7,451
EC 33	0	40,505	40,505	PL 10	490,571	746,735	1,237,306	ST 172	15,747	0	15,747
EC 33	0	37,820	37,820	PL 11	80,523	192	80,715	ST 173	0	67,618	67,618
EC 38	0	53,443	53,443	PL 12	113,448	52,877	166,325	ST 176	94,775	31,420	126,195
EC 42	0	395,577	395,577	PL 12	0	117	117	ST 193	0	29,313	29,313
EC 45	0	1,969	1,969	PL 13	81,085	160,631	241,716	ST 194	0	156,976	156,976
EC 46	598,675	2,663	601,338	PL 17	0	198,740	198,740	ST 195	0	97,650	97,650
EC 47	174,811	139,295	314,106	PL 18	91	26,527	26,618	SX 18	0	30,318	30,318
EC 48	0	475,399	475,399	PL 19	21,646	0	21,646	VR 21	0	7,214	7,214
EC 49	0	27,724	27,724	PL 20	222,099	0	222,099	VR 22	0	86,004	86,004
EC 56	0	23,284	23,284	PL 23	0	1,445,920	1,445,920	VR 38	4,723	5,217	9,940
EC 57	0	7,279	7,279	PL 24	0	425,296	425,296	VR 38	0	83,010	83,010
EC 64	319,063	854,947	1,174,010	SA 3	0	46,923	46,923	VR 39	0	259,653	259,653
EC 66	0	5,407	5,407	SA 6	0	1,945	1,945	VR 46	0	286,576	286,576
EC 67	0	242,894	242,894	SA 10	0	6,510	6,510	VR 54	0	8,756	8,756
EC 71	0	38,145	38,145	SA 13	681,708	0	681,708	VR 56	106,870	0	106,870
EC 72	0	27,023	27,023	SM 7	0	17,141	17,141	VR 57	0	9,340	9,340
EC 76	0	134,042	134,042	SM 8	3,282	0	3,282	VR 60	0	103,115	103,115
EC 81	0	551,745	551,745	SM 10	23,966	1,349	25,315	VR 65	0	2,729	2,729
EC 82	0	38,175	38,175	SM 11	143,241	493	143,734	VR 70	0	54,638	54,638
EC 82	0	6,507	6,507	SM 15	124,101	0	124,101	VR 78	0	5,197	5,197
EC 83	0	90,215	90,215	SM 16	52,868	0	52,868	VR 83	0	81,469	81,469
EC 84	0	20,785	20,785	SM 18	0	51,208	51,208	VR 84	0	464,526	464,526
EC 88	0	57,383	57,383	SM 22	0	3,266	3,266	VR 86	0	16,226	16,226
EC 89	122,270	27,863	150,133	SM 23	0	659,570	659,570	VR 100	0	21,774	21,774
EC 109	0	3,761	3,761	SM 24	113	5,436	5,549	VR 102	0	727	727
EC 129	0	2,564	2,564	SM 27	28,560	1,692	30,252	VR 114	0	55,579	55,579
EC 142	0	296	296	SM 28	0	6,319	6,319	VR 115	0	396	396
EC 143	0	1,502	1,502	SM 29	0	68,346	68,346	VR 116	0	38,314	38,314
EC 144	0	57,584	57,584	SM 33	104	262,826	262,930	VR 117	0	238	238
EC 148	0	44,578	44,578	SM 34	0	123,291	123,291	VR 119	36,717	310,101	346,818
EC 149	0	2,061	2,061	SM 35	124,443	0	124,443	VR 124	159,708	0	159,708
EC 151	0	52,133	52,133	SM 36	0	143,294	143,294	VR 128	0	46,755	46,755

Lease Block	Water from Oil Zones (bbl)	Water from Gas Zones (bbl)	Total Water (bbl)	Lease Block	Water from Oil Zones (bbl)	Water from Gas Zones (bbl)	Total Water (bbl)	Lease Block	Water from Oil Zones (bbl)	Water from Gas Zones (bbl)	Total Water (bbl)
EC 154	0	981	981	SM 37	0	235,559	235,559	VR 129	0	8,804	8,804
EC 157	0	1,054	1,054	SM 39	415,451	395,778	811,229	VR 131	0	670,397	670,397
EC 160	0	18,152	18,152	SM 48	0	8,826	8,826	VR 146	496,490	291,253	787,743
EC 161	0	508	508	SM 49	0	7,751	7,751	VR 156	0	128,905	128,905
EC 171	0	36,678	36,678	SM 61	0	29,771	29,771	VR 159	0	64,261	64,261
EC 172	0	27,862	27,862	SM 66	0	25,189	25,189	VR 160	0	5,401	5,401
EC 179	0	34,041	34,041	SM 76	0	10,390	10,390	VR 161	0	37,131	37,131
EC 184	0	532,540	532,540	SM 77	0	28,964	28,964	VR 164	26,505	2,866	29,371
EC 195	0	24,761	24,761	SM 78	0	12,671	12,671	VR 164	0	859	859
EC 196	0	41,374	41,374	SM 233	0	79,086	79,086	VR 175	0	69,166	69,166
EI 47	0	167,743	167,743	SM 234, 235	0	282,972	282,972	VR 182	1,204,805	0	1,204,805
EI 49	0	12,915	12,915	SM 235	0	13,974	13,974	VR 191	0	68,511	68,511
EI 50	0	68,147	68,147	SM 243	0	374	374	VR 201	86,560	0	86,560
EI 51	0	932,115	932,115	SM 244	0	421,328	421,328	WC 19	0	1,451	1,451
EI 64	0	28,365	28,365	SM 249	0	5,357	5,357	WC 35, 66	608,871	415	609,286
EI 71	0	97,574	97,574	SM 250	0	15,457	15,457	WC 44	0	10,241	10,241
EI 72	0	1,822	1,822	SM 252	0	8,031	8,031	WC 45	0	117,411	117,411
EI 74	0	42,150	42,150	SM 253	0	38	38	WC 46	0	68,365	68,365
EI 87	0	1,011	1,011	SM 255	0	114,882	114,882	WC 47	0	46,338	46,338
EI 88	29,715	0	29,715	SM 261	0	204,936	204,936	WC 53	0	138,749	138,749
EI 89	0	1,785	1,785	SM 268	71,091	10,143	81,234	WC 54	0	2,519	2,519
EI 95	332,446	73,479	405,925	SM 269	783,389	909,563	1,692,952	WC 60	0	19,047	19,047
EI 97	0	105,397	105,397	SM 275	0	37,609	37,609	WC 61	0	5,798	5,798
EI 99	0	2,232	2,232	SM 280	0	14,903	14,903	WC 65	178,371	210,656	389,027
EI 100	1,271,180	149,248	1,420,428	SM 281	1,244,955	2,045,633	3,290,588	WC 66	156,523	614,388	770,911
EI 105	886,106	197,552	1,083,658	SM 288	454,327	263,288	717,615	WC 67	75,243	0	75,243
EI 106	43,003	89,790	132,793	SS 58	170,987	0	170,987	WC 68	0	177,849	177,849
EI 107	0	94,750	94,750	SS 59	47,909	152,529	200,438	WC 71	0	18,397	18,397
EI 108	0	267,817	267,817	SS 63	0	2,526	2,526	WC 72	0	27,806	27,806
EI 110	0	777	777	SS 65, 66	606,781	56,190	662,971	WC 73	0	538	538
EI 113A	0	22	22	SS 68	545,474	20,128	565,602	WC 76	0	603,029	603,029
EI 116	113,367	0	113,367	SS 69	1,214,077	80,127	1,294,204	WC 77	0	103,692	103,692
EI 118	0	334,384	334,384	SS 72	203,687	426,745	630,432	WC 91	0	98,670	98,670
EI 119	1,272,435	18,678	1,291,113	SS 72	1,992	6,972	8,964	WC 98	0	69,876	69,876
EI 120	2,145,159	275,866	2,421,025	SS 76	129,681	42,568	172,249	WC 100	0	63,245	63,245
EI 125	28,219	0	28,219	SS 79	0	33,837	33,837	WC 101	0	185,154	185,154
EI 126	1,012,749	0	1,012,749	SS 87	0	774,294	774,294	WC 102	0	300,796	300,796
EI 128	594,230	0	594,230	SS 91	371,285	96,281	467,566	WC 110	0	49,966	49,966

Lease Block	Water from Oil Zones (bbl)	Water from Gas Zones (bbl)	Total Water (bbl)	Lease Block	Water from Oil Zones (bbl)	Water from Gas Zones (bbl)	Total Water (bbl)	Lease Block	Water from Oil Zones (bbl)	Water from Gas Zones (bbl)	Total Water (bbl)
EI 128A	229,284	255,255	484,539	SS 92	0	42,121	42,121	WC 111	0	6,059	6,059
EI 129	354,169	4,803	358,972	SS 93	236,706	26,314	263,020	WC 116	0	258,674	258,674
EI 133	2,794	13,089	15,883	SS 100	883,725	0	883,725	WC 118	3,131	103,366	106,497
EI 135	0	39,816	39,816	SS 103	0	88,671	88,671	WC 130	0	7,371	7,371
EI 136	0	28,829	28,829	SS 105	0	641,889	641,889	WC 132	0	273	273
EI 142	1,569	0	1,569	SS 108	1,453,569	0	1,453,569	WC 142	0	2,365	2,365
EI 143	0	3,797	3,797	SS 112	102,219	165,186	267,405	WC 143	0	35,164	35,164
EI 147	0	229,209	229,209	SS 113	993	1,431	2,424	WC 144	0	129,328	129,328
EI 148	0	164	164	SS 114	65,845	74,369	140,214	WC 146	0	7,931	7,931
EI 156	0	6,394	6,394	SS 117	189,426	0	189,426	WC 148	0	154,013	154,013
EI 157	0	33,291	33,291	SS 126	0	1,046,529	1,046,529	WC 149	0	367	367
EI 158	822,454	449,740	1,272,194	SS 129	2,472	93,790	96,262	WC 150	0	11,844	11,844
EI 159	0	275	275	SS 130	0	168	168	WC 152	0	25,660	25,660
EI 162	0	57,756	57,756	SS 133	0	4,837	4,837	WC 153	0	51,092	51,092
EI 163	0	3,946	3,946	SS 139	0	168,530	168,530	WC 163	0	902	902
EI 167	10,536	0	10,536	SS 148	10,413	241	10,654	WC 165	0	106	106
EI 172	0	5,606	5,606	SS 149	258,608	28,585	287,193	WC 168	0	13,308	13,308
EI 173	411,323	0	411,323	SS 150	183,176	55,564	238,740	WC 170	0	2,292,199	2,292,199
EI 174	80,555	25,663	106,218	SS 151	92,706	0	92,706	WC 171	0	5,812	5,812
EI 175	193,386	333,943	527,329	SS 154	686,375	816,637	1,503,012	WC 172	0	3,535	3,535
EI 176	20,481	0	20,481	SS 156	193,598	0	193,598	WC 173	0	103,717	103,717
EI 177	0	4,786	4,786	SS 157	0	3,362	3,362	WC 176	8,450	2,020	10,470
EI 181	100,040	0	100,040	SS 159	0	216,208	216,208	WC 178	97,555	0	97,555
EI 182	194,944	134,432	329,376	SS 166	0	3,962	3,962	WC 180	0	206,770	206,770
EI 183	215,879	0	215,879	SS 168	0	14,527	14,527	WC 182	0	74,154	74,154
EI 184	1,611,791	0	1,611,791	SS 169	897,323	132,134	1,029,457	WC 191	0	1,146	1,146
EI 187	0	11,695	11,695	SS 170	0	249	249	WC 192	0	99,333	99,333
EI 188	662,405	0	662,405	SS 171	169,422	0	169,422	WC 193	0	127,393	127,393
EI 189	324,328	382,420	706,748	SS 175	118,988	0	118,988	WC 194	0	146,298	146,298
EI 190	0	216	216	SS 177	128,102	0	128,102	WC 195	0	4,189	4,189
EI 193	199,493	213,926	413,419	SS 178	579,977	147,930	727,907	WC 196	0	21,091	21,091
EI 196	0	75,433	75,433	SS 181	1,129,471	226,527	1,355,998	WC 197	0	20,435	20,435
EI 196	0	42	42	SS 182	1,634,645	0	1,634,645	WC 198	0	103,750	103,750
EI 198	0	14,447	14,447	SS 182	530,594	94,476	625,070	WC 206	0	31,345	31,345
EI 199	0	5,619	5,619	SS 183	1,433,862	95,119	1,528,981	WC 210	0	506	506
EI 202	0	179,446	179,446	SS 184	0	18,109	18,109	WC 215	568,702	3,244	571,946
EI 203	0	406	406	SS 187	0	116,337	116,337	WC 222	0	3,585	3,585
EI 205	0	452,181	452,181	SS 189	0	382,254	382,254	WC 225	0	108,386	108,386
EI 206	0	6	6	SS 190	0	270,784	270,784	WC 226	0	5,049	5,049
EI 208	722,390	0	722,390	SS 191	0	154,259	154,259	WC 229	0	176,099	176,099
EI 211	76,647	0	76,647	SS 193	1,153,791	23	1,153,814	WC 238	0	9,816	9,816

Lease Block	Water from Oil Zones (bbl)	Water from Gas Zones (bbl)	Total Water (bbl)		Lease Block	Water from Oil Zones (bbl)	Water from Gas Zones (bbl)	Total Water (bbl)		Lease Block	Water from Oil Zones (bbl)	Water from Gas Zones (bbl)	Total Water (bbl)
EI 212	0	427,763	427,763		SS 194	87,683	0	87,683		WC 239	0	35,289	35,289
EI 214	0	39,333	39,333		SS 198	332,246	352,473	684,719		WC 248	0	58,746	58,746
EI 215	137,107	0	137,107		SS 198	110,547	787,699	898,246		WC 269	0	2,056	2,056
EI 217	0	525	525		SS 206	422,638	0	422,638		WC 289	0	4,645	4,645
EI 218	8,234	0	8,234		SS 207	1,664,805	162,794	1,827,599		WC 290	0	272	272
EI 224	34,518	171,899	206,417		SS 208	779,501	17,089	796,590		WC 291	0	69,522	69,522
EI 229	0	2,681	2,681		SS 214	194,952	158,296	353,248		WC 293	0	1,292	1,292
EI 230	0	10,028	10,028		SS 215	167,597	5,004	172,601		WC 294	0	885,697	885,697
EI 231	0	840	840		SS 216	0	1,442,582	1,442,582		WC 300	0	19,437	19,437
EI 237	143,240	6,975	150,215		ST 21	3,524,548	252,963	3,777,511		WC 304	0	315	315
EI 238	0	5,817	5,817		ST 22	1,721,085	29,792	1,750,877		WC 310	0	5,677	5,677
EI 240	29,689	34,901	64,590		ST 23	942,041	0	942,041		WC 313	0	6,436	6,436
EI 242	0	7,391	7,391		ST 23	1,619,003	0	1,619,003		WC 315	0	23,032	23,032
EI 243	0	1,137,471	1,137,471		ST 24	1,728,171	0	1,728,171		WC 331	0	58	58
GI 17	1,624	0	1,624		ST 26	352,376	0	352,376		WC 343	0	96,601	96,601
GI 18	79,354	0	79,354		ST 26	1,765,655	199,781	1,965,436		WC 347	0	29,044	29,044
GI 19	806,935	0	806,935		ST 27	16,261	0	16,261		WD 21	0	16,373	16,373
GI 20	0	14,752	14,752		ST 28	0	198	198		WD 23	0	10,413	10,413
GI 21, 30	160,466	0	160,466		ST 35	795,012	65,980	860,992		WD 24	223,216	111,376	334,592
GI 22	2,164,101	0	2,164,101		ST 36	236,362	264,740	501,102		WD 27	981,193	188,315	1,169,508
GI 23	3,591,721	0	3,591,721		ST 37	5,547,354	1,280,793	6,828,147		WD 28	144,936	7,865	152,801
GI 26	588,405	0	588,405		ST 38	0	136,096	136,096		WD 29	2,186,488	7,757	2,194,245
GI 28	0	226	226		ST 48	0	254,749	254,749		WD 30	8,215,453	0	8,215,453
GI 32	463,811	334,104	797,915		ST 51	3,189,226	253,472	3,442,698		WD 31	2,595,223	0	2,595,223
GI 32	372,632	240,214	612,846		ST 52	2,433,453	38,811	2,472,264		WD 32	745,268	9,132	754,400
GI 33	643,575	175,730	819,305		ST 53	4,414,797	0	4,414,797		WD 32	77,669	0	77,669
GI 37	910,964	0	910,964		ST 54	2,127,092	11,369	2,138,461		WD 32	262,035	0	262,035
GI 40	2,063,561	48,530	2,112,091		ST 55	0	32,364	32,364		WD 34	0	291,696	291,696
GI 41	1,888,323	158,281	2,046,604		ST 63	0	59,229	59,229		WD 35	0	205,785	205,785
GI 41	0	1,497,091	1,497,091		ST 66	1,759	0	1,759		WD 38	34,592	0	34,592
GI 42	162,771	7,582	170,353		ST 67	1,593,028	45,255	1,638,283		WD 39	0	2,284	2,284
GI 43	0	222,269	222,269		ST 68	270,659	0	270,659		WD 41	95,725	709,390	805,115
GI 45	0	23,277	23,277		ST 71	0	171,459	171,459		WD 44	167,993	862,241	1,030,234
GI 46	0	246,375	246,375		ST 72	199,348	61,839	261,187		WD 45	1,673,021	134,876	1,807,897
GI 47	2,525,220	144,064	2,669,284		ST 76	0	152,197	152,197		WD 58	0	1,490,896	1,490,896
GI 48	506,412	176,548	682,960		ST 77	0	221,663	221,663		WD 59	0	94,428	94,428
GI 52	0	760,439	760,439		ST 99	0	21	21		WD 61	0	552,357	552,357
HI 36	0	4,331	4,331		ST 100	0	376,893	376,893		WD 63	0	176,436	176,436
HI 37	0	4,339	4,339		ST 107	0	6,717	6,717		WD 65	0	21,737	21,737
HI 38	0	5,153	5,153		ST 111	0	96	96		WD 68	0	23,234	23,234
HI 39	0	8,725	8,725		ST 112	0	33,658	33,658		WD 70	3,450,635	374,179	3,824,814

Lease Block	Water from Oil Zones (bbl)	Water from Gas Zones (bbl)	Total Water (bbl)		Lease Block	Water from Oil Zones (bbl)	Water from Gas Zones (bbl)	Total Water (bbl)		Lease Block	Water from Oil Zones (bbl)	Water from Gas Zones (bbl)	Total Water (bbl)
HI 45	0	6,012	6,012		ST 128	0	33,503	33,503		WD 71	1,650,267	302,976	1,953,243
HI 47	0	1,942	1,942		ST 130	326,389	0	326,389		WD 72	0	25,920	25,920
HI 72	0	32,837	32,837		ST 139	0	8,448	8,448		WD 73	1,408,764	371,734	1,780,498
HI 84	0	5,372	5,372		ST 143	0	3,611	3,611		WD 74	3,007,589	58	3,007,647
HI 85	0	51,062	51,062		ST 146	0	1,065	1,065		WD 95	1,781,786	36,100	1,817,886
HI 129	0	42,640	42,640		ST 148	734,268	54,615	788,883		WD 96	555,012	0	555,012
HI 166	0	1,650	1,650		ST 148	0	145,664	145,664					
HI 167	0	478,170	478,170		ST 161	0	24,684	24,684					

Total Water from Oil Zones = 125,122,378 bbl/year
Total Water from Gas Zones = 60,199,843 bbl/year
Total Water = 185,322,221 bbl/year